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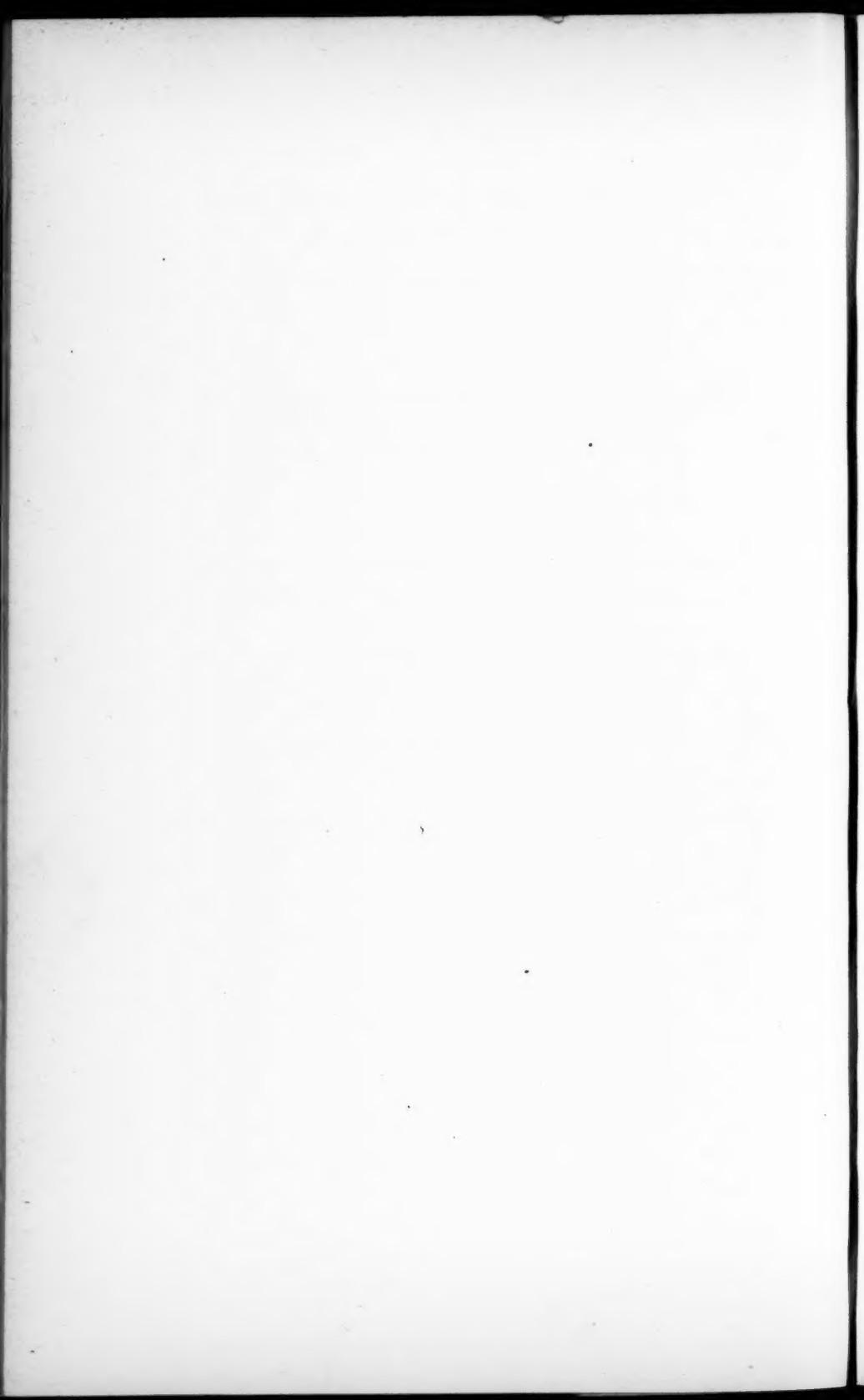
CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF  
PHYSICAL CHEMISTRY OF THE MASSACHUSETTS  
INSTITUTE OF TECHNOLOGY.—No. 1.

*THE ELECTRICAL CONDUCTIVITY OF AQUEOUS  
SOLUTIONS AT HIGH TEMPERATURES.*

1.—*DESCRIPTION OF THE APPARATUS. RESULTS WITH  
SODIUM AND POTASSIUM CHLORIDE UP TO 306°.*

BY ARTHUR A. NOYES AND WILLIAM D. COOLIDGE.

INVESTIGATIONS ON LIGHT AND HEAT MADE OR PUBLISHED, WHOLLY OR IN PART, WITH APPROPRIATIONS  
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I. PLAN OF THE INVESTIGATION.

ONLY a few isolated experiments have been previously published on the electrical conductivity of salt solutions above 100°. Sack \* investigated the conductivity of three copper sulphate solutions up to 120°. Maltby † found that upon heating up to 237° the conductivity of an aqueous potassium chloride solution steadily diminished. Hagenbach ‡

\* Wied. Ann., **43**, 212–224 (1891).

† Ztschr. phys. Chem., **18**, 155 (1895).

‡ Drude's Ann., **5**, 276–312 (1901).

observed a maximum in the molecular conductivity of a 0.01 normal KCl solution. In all of these experiments the conductivity cell was made of glass and was necessarily very small; therefore, owing to the solubility of glass at these temperatures and to the danger of polarization of the small electrodes used, the results have little significance.

Believing that accurate conductivity measurements through a wide range of temperature extending up to or nearly to the critical point would yield results of considerable theoretical interest, we have undertaken an investigation in this direction.

The first and most difficult part of this research consisted in the construction of a conductivity cell composed internally of material unacted upon by aqueous solutions and capable of withstanding without leakage the high vapor-pressure of such solutions up to the critical temperature. After working continuously for three years upon this problem, we have succeeded in overcoming the mechanical difficulties and in constructing a platinum-lined bomb with insulated electrodes which remains perfectly tight at any rate up to 306°, which occasions only an unimportant contamination even in salt solutions as dilute as  $\frac{1}{2000}$  molar, which yields conductivity measurements accurate to 0.25 per cent or less, and which at the same time makes possible specific-volume determinations, which are essential to the interpretation of the results. Now that a knowledge of the necessary mechanical devices has been acquired, the making of such a bomb is an easy task for a skilled instrument maker. We shall, therefore, in this article first describe in full detail, with the help of working drawings, the apparatus used, and especially the construction of the bomb, in order to make it readily available for investigators who desire to pursue researches of the same kind or those requiring similar apparatus (such, for example, as a calorimetric bomb).

We have thus far been able to investigate only two dissolved substances,—potassium and sodium chloride,—but have made conductivity and specific volume measurements with their solutions at various temperatures ranging from 26° to 306° and at various concentrations between 0.1 and 0.0005 molar. The work will be extended during the coming year to other substances, and if possible to the critical temperature; but as it will be carried on in part by other workers and under the auspices of the Carnegie Institution, it has seemed appropriate to publish the results already obtained, especially as these seem to justify several interesting conclusions of a general character.

In concluding these introductory statements it gives us much pleasure to acknowledge our great indebtedness to the American Academy of

Arts and Sciences, which by liberal grants made from the Rumford Fund of the Academy has given us substantial assistance in meeting the considerable expense involved in this investigation.

## II. DESCRIPTION OF THE APPARATUS.

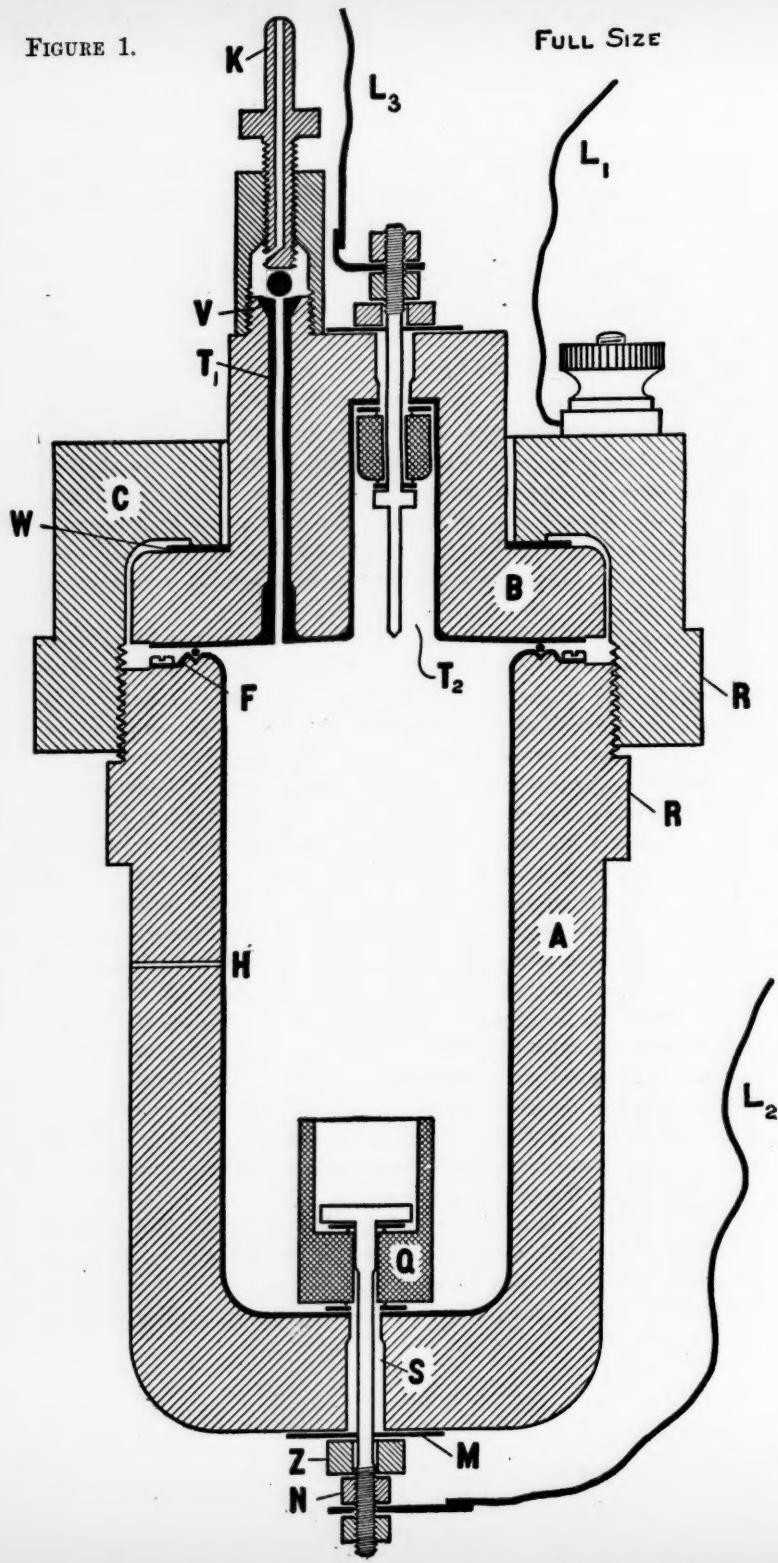
1. *The Conductivity Cell or Bomb.*—A vertical section of this is shown in full size in Fig. 1. It is a cylindrical vessel, A, with a cover, B, which is held in place by the large nut, C. A, B, and C are made of soft crucible steel. To prevent contamination, the bomb is lined throughout with sheet platinum 0.41 mm. thick. The cover joint is made tight by a little packing ring, made of pure gold wire, which fits into a shallow V-shaped groove. As may be seen in the diagram, the platinum lining, indicated by a heavy line, goes under this ring and a little distance beyond it, the outer edge being fastened to the shell by eight small steel screws, of which two are shown. The lower vessel has a capacity of about 122 ccm.

The body of the bomb serves as one electrode, connection being made with it by means of the large binding post on top of the nut C. The second electrode is brought in through the bottom of the bomb and is insulated from the latter by means of the mica washer, M, the air space, S, and the quartz-crystal piece, Q. The body of this electrode is of steel, but its upper part is covered with sheet platinum. On the bottom of the crystal piece is turned a single sharp V-shaped ridge, and this rests on a flat gold washer which is inserted between the crystal and the bottom of the bomb. Another gold washer is placed between the upper part of the electrode and a second V-shaped ridge turned on the upper face of the crystal. The nut N, fitting on the lower, threaded end of the electrode, draws the latter down, thus forcing the ridges of the crystal into the soft gold and making the joints tight. Z is a brass washer which by its greater expansion-coefficient makes up for the difference in the expansion, upon heating, of the quartz-crystal and of that part of the steel electrode which lies within. The second nut, on the lower end of the electrode, serves to bolt on a small copper tag to which the wire L<sub>2</sub> is silver-soldered. The quartz piece, Q, is extended in the form of a cup above the electrode, so as to increase the resistance-capacity of the cell.

In the cover, B, is a narrow cylindrical chamber provided with an "auxiliary electrode," which is insulated in just the same way as the lower electrode. The purpose of this small chamber with the auxiliary electrode is twofold: first, it serves as a safety device, showing that the

FIGURE 1.

FULL SIZE



bomb has not become completely full of liquid; and secondly, it furnishes a means of measuring the specific volume of the solutions. The first provision is necessary since the bomb is designed to withstand the vapor pressure, but not the fluid pressure of the liquid. A knowledge of the specific volume is required in order to calculate the equivalent from the observed conductivity. A measurement of the resistance between  $L_1$  and  $L_3$ , together with a measurement of that between  $L_1$  and  $L_2$  when preceded by a calibration which may be made once for all, shows, as will be explained more fully in Section VI., at any time after the solution has expanded sufficiently to come into contact with the auxiliary electrode, just how high the liquid stands, and therefore how much vapor space remains.

The small platinum tube,  $T_1$ , serves to exhaust the air from the bomb. The method of doing this will be apparent from the diagram and the following description. The hollow screw  $K$  is connected by means of rubber tubing with a Richards water pump, and is at first raised so that air can come out under the little steel bicycle ball which rests on the upper end of the platinum tube. After the air is removed until a pressure gauge shows a pressure within of about 2 cm., and while the pump is still in operation, the part  $K$  is screwed down, thus forcing the steel ball onto its seat and closing the end of the tube.

The solution comes into contact with nothing but platinum, quartz-crystal, and gold, except at the top of the narrow tube,  $T_1$ , where it may touch the steel ball. The latter could be gold plated; but this has proved unnecessary, since there is scarcely any circulation through the narrow tube.

The lower electrode, as well as the auxiliary electrode and its surrounding tube, are well platinized. The body of the lining is not platinized, since on account of its great surface this is not necessary.

2. *The Conductivity Measuring Apparatus.*—The conductivity was measured by the ordinary Kohlrausch-Wheatstone Bridge method, using the induction coil and telephone. The slide wire was of platinum-iridium; it was one meter in length and 0.4 mm. in diameter. The resistance coils, 2000 ohms in all (or 4000 ohms in a few measurements), were of manganine. The whole conductivity apparatus was mounted on a small portable table so that it could be moved about as the bomb was changed from one heating bath to another. It was always kept at a distance from the heaters. No temperature correction needed to be applied to the resistance coils. Heavy flexible copper leads were used up to within a few centimeters of the top of the heaters, where they were

joined by means of brass connectors to the smaller copper wires,  $L_1$ ,  $L_2$ ,  $L_3$ , coming from the bomb. A double-throw switch served to connect the conductivity apparatus with  $L_1$  and  $L_2$  or with  $L_1$  and  $L_3$ .

3. *The Heaters.*—Conductivity measurements were made at about  $26^\circ$ ,  $140^\circ$ ,  $218^\circ$ ,  $281^\circ$ , and  $306^\circ$ . The first of these temperatures was attained by immersing the bomb in a bath of commercial xylene contained in a double-walled, well-jacketed, metal cylinder. This substance has the advantages that it is a good insulator, non-corrosive, and not very volatile, and that the bomb can be transferred from it directly, without cleaning, into the xylene-vapor bath by which the next higher temperature was attained. The liquid was stirred by a small propeller, and was heated electrically at will with the help of a platinum helix immersed in it.

For all the higher temperatures, vapor baths were employed, as these furnish the only safe and rapid method of heating. The temperature adjusts itself automatically, and can never rise much above the ordinary boiling point, thus giving protection against overheating and undue expansion of the liquid within the bomb, which by completely filling it might cause it to burst. Moreover, if the bomb should spring a leak, it would be dangerous in the case of a liquid bath; for the steam, escaping under such pressure, might throw some of the hot liquid onto the observer. Steam leaking out into the hot vapor, on the other hand, causes no annoyance further than that arising from the odor of the vapor and the loss of the material in the case of the expensive substances. An air bath would, of course, not be open to this objection; but the heating would be extremely slow and non-automatic.

An elevation of one of the heaters,—all of which were substantially alike,—with the bomb in place is presented in Fig. 2. The bath is made of a piece of wrought-iron pipe, A, 16 cm. in diameter and 40 cm. long, with a bottom piece welded in. Near the top two pieces of iron pipe, C, about 2 cm. in diameter and 25 cm. long are screwed in, to serve as condensers. These condenser tubes are given a slight pitch, but their outer ends should not be higher than the top of the heater. To increase their efficiency, a loose roll of iron wire gauze is put into each of them. The top of the bath, which should be turned off square in the lathe, is covered with a large watch glass, D, in which holes are drilled for the thermometer, T, and the lead-wires to the bomb. A tube of thin sheet iron, Q, about 12 cm. in diameter, with a flange at the bottom, is placed in the heater and held in the middle by projecting pins. Small holes are drilled through this tube at the bottom, and two rows of large

holes at the top. The function of this tube is to prevent the bottom of the bomb from getting hotter than the top; for, if it does this by ever so little, a constant evaporation and condensation goes on in the bomb, which

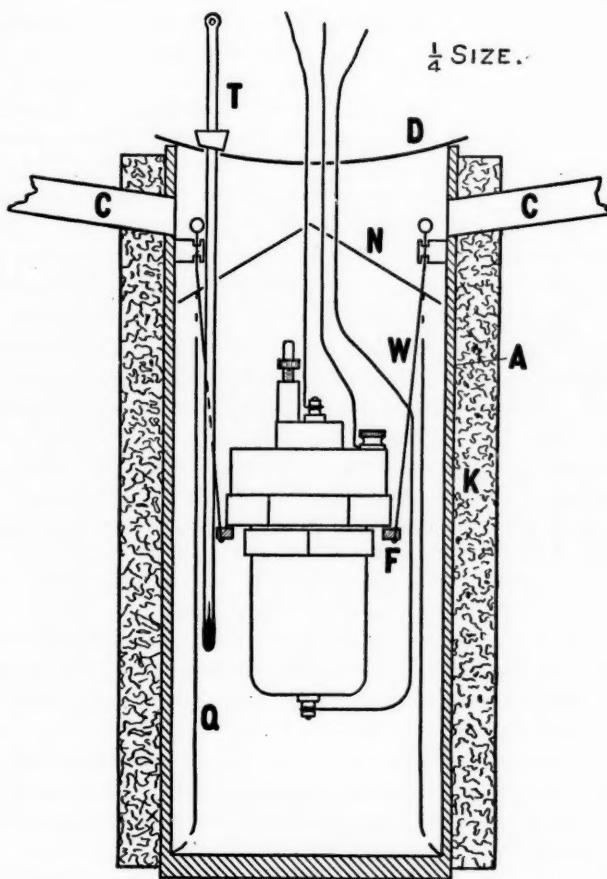


FIGURE 2.

interferes with the readings of the auxiliary electrode and the specific-volume determinations. The inverted mica cone, N, is put in for the same purpose: it prevents the cold condensed vapor from dripping onto the top of the bomb. These arrangements also protect the bomb more effectually

from radiation and convection-currents from the walls of the heater. The holes in the glass cover through which the lead-wires and the thermometer enter are but little larger than these, so as to prevent loss of vapor. The thermometer is supported by means of a cork stopper which rests on the top of the watch glass. The insertion of cork stoppers in the holes is not advisable, as they cause the hot liquid to escape through their pores. The bomb is supported in the heater by means of a brass frame, F, and suspension wires, W, which hang on two steel pins screwed into the walls of the heater. At the top of each of the two suspension wires is a loop, so that by inserting a steel hook in each of these loops, the bomb is easily removed from the bath while still hot. The sides of the heater are well jacketed with asbestos. It is supported on a metal tripod by means of three steel pins, which project through the asbestos covering. It is heated by gas burners below, one sufficing after the bomb and heater have become hot.

Commercial xylene was first used for the 140° bath, but the pure metaxyleno was found to give a more constant temperature and one more uniform in the upper and lower parts of the bomb: to prevent the escape of the vapor, it was necessary in this case to cause water to circulate through a jacket surrounding one of the condenser tubes. Pure naphthalene from Kahlbaum was used to give a temperature of 218°, and was found to be an ideal substance. *a*-bromnaphthalene was employed for the next higher temperature (281°), as it seemed to be the only available substance; it is not convenient, however, since it decomposes slowly upon boiling with formation of tar and hydrobromic acid (which attacks the outside of the bomb): it must therefore be frequently removed from the heater and redistilled. The highest temperature (306°) was maintained with benzophenone, which boils unchanged even after many days of continuous heating.

4. *Thermometers.*—The temperature of the liquid xylene bath was measured with an ordinary thermometer reading directly to tenths of a degree, and this was checked from time to time against a standard Tonnelot thermometer.

For the higher temperatures French mercurial thermometers, made by Alvergniat, with a range of 360° and graduation in degrees, were used. By the use of a little reading telescope these thermometers were read with certainty to 0.1°. They were standardized as described in Section VI of this article. The mercury column was always completely immersed in the vapor, and to take a reading the thermometer was quickly raised only enough to render the meniscus visible above the top

of the heater. Repeated trials showed that the temperature of the bath throughout the space surrounding the bomb varied less than  $0.1^{\circ}$ , so that the exact position of the thermometer made no difference. Care had to be taken, however, that the mica shield above the bomb did not come in contact with the thermometer stem, thus allowing the condensed vapor coming from the shield to run down and cool the bulb. It was feared that the vapor condensing on the upper part of the thermometer itself would have the same effect; but this was proved not to be the case by fastening a small inverted watch glass about midway on the thermometer stem; this carried off the drip from the upper part of the stem, but did not affect the reading.

### III. DETAILS OF THE CONSTRUCTION OF THE BOMB.

The shell is made of the softest crucible-steel obtainable, because ductility is desired rather than high tensile strength.\* Extra weight is not objectionable here, as it would be in the case of a calorimetric bomb; moreover, fear was entertained that a high-carbon steel might be weakened by the repeated heating and cooling to which the bomb was to be subjected. The shell was designed for approximately equal strength throughout. The existing data on the tensile-strength of steel at the high temperatures involved only suffice to show that it is considerably weaker than at ordinary temperature. Owing to this fact, and to the further fact that it was uncertain to how high a temperature the observations would ultimately be carried, a factor of safety of 20-fold was allowed, based upon the tensile strength cold and the critical pressure of water-vapor. The large nut, C, has an ordinary V-thread of 18 turns to the inch. To tighten the nut, the lower part of the bomb is held at R, which is hexagonal, by a wrench bolted to a firm table; while a second wrench, with an effective length of 46 centimeters, is placed on the hexagonal part, R', of the nut itself. In this way sufficient pressure can be exerted on the gold packing ring to make the metal of which it is composed actually flow into the groove beneath, filling any little scratches or other depressions which may exist in the latter. Since there is a certain thickness of gold and platinum interposed between the cover and the lower part of the bomb, and since these both expand less than steel upon heating, it becomes necessary to use a compensating brass washer, W, between the nut and the cover. The proper thickness can be calculated from the

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\* Bessemer steel would probably be somewhat safer and will be used in future work.

known coefficients of expansion of the three metals. Care must be taken that the bearing surface of the nut, C, on the washer, W, is so large that the upward force of the steam acting on the cover does not compress the brass washer, and thus allow the cover to rise. Care must also be taken, — and this is very important, — that the distance from the centre of this bearing surface to the axis of the bomb is less than the radius of the gold packing ring; otherwise the cover might turn on the ring while the nut was being tightened, which would prevent a tight joint from being secured. Various lubricants have been tried on the screw and on the top of the brass washer; but all of these, with the exception of graphite, have proved to be worse than nothing: finely powdered graphite used dry is entirely satisfactory, however.

To facilitate the removal of the platinum lining, the inside of the steel shell was made slightly tapering (about 0.05 mm. in 10 cm.), and the little grooves left by the boring tool were carefully ground out.

In working with the bomb it proved to be necessary to drill a number of small holes through the steel shell, one of which is shown at H in Fig. 1. In the present bomb there are about 75 of these (probably half as many would have sufficed) well distributed over all its parts, A, B, and C. These holes are 0.66 mm. in diameter, — so small that they do not seriously weaken the shell, and that the platinum lining is capable of withstanding the pressure over their areas. These holes are made necessary by the fact that without them some water gets trapped between the lining and the shell, owing to slight leakage or permeation of the platinum itself when the bomb is first heated, the lining then being not in close contact with the shell at every point; and this water on subsequent heating exerts, owing to its expansion in the liquid state, an enormous pressure against the lining, causing little indentations in it and causing some water to flow back into the bomb, whereby contamination of the solution with iron is produced. The holes remedy entirely this difficulty, which otherwise becomes aggravated on each successive heating.

The lining of the lower part of the bomb, A, was made of a platinum-iridium alloy (2 per cent iridium) 0.40 mm. thick; but pure platinum would have been preferable, owing to its greater ductility, and it will be used in future work. The lining was made by Baker & Company of Newark, N. J. The flange, F, was originally made of the same material, but the closing of the bomb compressed the platinum each time under the ring so that it grew hard and thin and finally cracked at the bottom of the groove. For this reason platinum-iridium alloy containing 15 per cent of iridium had to be substituted for the flange. This is so hard that

it bids fair to wear indefinitely, and yet it is not so brittle that it cannot be forced into the groove in the steel without cracking. The flange could probably just as well be welded to the platinum cup, but in our bomb it was soldered to it with pure gold. Pure gold was also used freely in making repairs on the present lining when it tore, as it frequently did at the start before the necessity of the small holes in the shell and of several other precautions was understood. In the measurements made so far the gold has exerted no deleterious influence.

The lining is made so as to fit as well as possible at the start. It is then inserted in the shell, the latter is placed in the lathe, and by means of a steel or agate burnisher the lining is spun in. This brings the lining for the most part in contact with the steel, but nothing can be done at the bottom in this way. By means of a piece of soft wood and a mallet, however, the bottom also can be made to fit closely. The flange at the top is now spun over in the lathe. The stiff alloy is easily and safely brought down into the sharp groove by proceeding as follows: One end of a short piece of brass rod 3 or 4 mm. in diameter is filed to a sharp V. Using this and a small hammer, the platinum can be driven down almost to the bottom of the groove. After every half dozen strokes the brass V will have to be sharpened. The brass is considerably softer than the alloy, and so does it no damage. Other methods have been tried, such as forcing a ring of hard-drawn copper wire down onto the platinum over the groove by means of the cover B and the large nut C. But the former method, although a little tedious, is much better. The sides of the groove in the steel make an angle of  $90^{\circ}$  with each other, and its depth is such that when a wire 0.8 mm. in diameter is laid in it, about one half of the wire lies outside the groove.

After the lining has been made to fit as closely as possible, it should be removed from the shell and heated to redness to anneal it. Even the flange had better be treated in this way, since it is hard enough even after annealing. To remove the lining after it has been fitted in in the preceding manner, the following plan was adopted: Take a stick of soft wood, perhaps 20 cm. long and 5 cm. square, and whittle one end down so that it will slip easily into the bomb. Then take a piece of cotton cloth moistened with alcohol to remove any grease, wrap it over the small end of the stick, and then with a hammer drive the latter tightly into the bomb. Now holding the bomb in the vise, grasp the projecting end of the stick firmly in the hands and twist out the lining. This method never fails, provided the steel shell was ground reasonably smooth at the start.

To remove the lining after the bomb has once been heated is a much more difficult matter. It can be accomplished without lasting injury to the platinum cup, but it necessitates a new flange. The flange is bent up into line with the cup at three points, and at these points a long piece of steel, about the size of a lead pencil and preferably elliptical in cross section, with its entering end ground down to a blunt wedge (with edges carefully rounded), is forced in between the lining and the shell. The lining along three lines parallel to the axis of the cylinder and extending nearly to the bottom is then pried in toward the centre. This loosens the cup so that it can be removed by hand. The lining can then be straightened out, the adhering iron and ferric oxide removed by the use of melted acid potassium sulphate, any needed repairs made, and a new flange put on. The removal of the lining would



FIGURE 3.

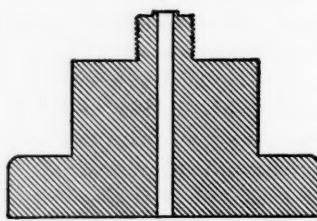


FIGURE 4.

doubtless be made easier by making the shell much more tapering; but this is very undesirable because it greatly increases, for a given volume of the bomb, the difficulty of securing a tight joint at the cover. It is, moreover, unnecessary, because if these instructions are followed carefully there should be no need of removing the lining after it is once finally in place.

A hole is drilled in the lining at the bottom so as to correspond with the hole in the steel shell. It is then best to close this hole temporarily with the steel piece shown in Fig. 3, using a lead washer under the V-shaped ridge for packing. Then, in order to bring the lining into perfect contact with the shell and at the same time to test it for possible faults, the lower part of the bomb is connected by means of the auxiliary cover shown in Fig. 4 with a Cailletet pump or its equivalent,—a water reservoir being interposed between the pump and bomb so as to force water instead of oil into the bomb. For this testing of the lining a

pressure of 300 atmospheres has been used, the steel shell having previously been similarly tested up to 600 atmospheres pressure. The lining must be fitted as closely as possible before the hydraulic pressure is applied, since otherwise this will always result in tearing the lining. Even after expanding the lining with hydraulic pressure, there is no trouble in removing it, in case a leak develops, by the first method given above.

The next step is to fasten the edge of the flange to the shell. If this is not done, when substances like benzophenone, solid at ordinary temperature, are employed for heating the bomb, they will be drawn under the flange and into the groove in the shell, where they will solidify; upon heating the bomb the next time, the solid melts and escapes, thus relieving the pressure on the packing ring and allowing the bomb to leak: moreover, if the edge is not fastened down, there is danger of bending it when the bomb is opened and handled. To secure the flange eight small steel screws are used. The steel shell has to be recessed at this place, as shown in Fig. 1; otherwise the screw heads would interfere with the cover.

The lower electrode is made of two steel parts, as shown in Fig. 5, the horizontal part, C, being afterwards enclosed in a platinum box, which is made as follows: The top, A, of this box is made by forcing a circular disk of pure sheet platinum (about 0.25 mm. thick) through a brass die by means of a brass punch. It is better, since it strains the platinum less, to interrupt this operation at least twice, annealing the metal each time. This box should be made to fit so tightly over C that it has to be forced on. In the same way a tight fitting bottom, B, is made for this box. A hole is drilled in the centre of this just large enough to permit the passage of the steel rod through it. It is then forced on over A. It then remains only to solder B to A with pure gold. This is easily accomplished by putting several pieces of gold on the crack, D, and directing a hot flame from the blast lamp downwards onto the box. This flame must not be too small, since the whole of the soldering must be done at once and as quickly as possible. Doing it a piece at a time involves keeping the steel rod hot for a longer time, and consequently

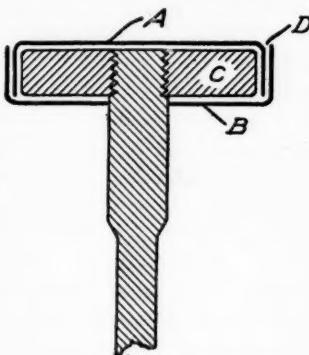


FIGURE 5.

oxidizing it more; and worse than this, the gold gets inside and alloys with the iron, bringing the latter eventually to the surface. Before soldering it is better to cover the steel rod below the box with pieces of asbestos, binding them on tightly by means of a wire, so as to diminish the oxidation.

Before adopting quartz crystal as the insulator various other substances were tried. Mica was tried first of all, using both of the methods subsequently employed by Knipp\* in his work on surface tension. Our experience agreed with his,—that it is impossible to secure an absolutely tight joint with mica because of the formation of radial cracks. Nor was it an ideal substance chemically. Carnelian, flint, and agate were next tried because of their known toughness. It was with the last-named substance that we developed the method finally employed for making an absolutely tight joint; the substance itself, however, proved to be chemically unsuitable, since the hydrated silica which it contains dissolves readily in the hot water. The method which we finally employed for securing a tight joint put very little strain on the agate, so that there was no longer any reason for avoiding a substance because of its brittleness. Quartz crystal was then the natural substance to try. Japanese quartz, however, proved a failure, owing to included water or carbon dioxide, which caused it to crack upon heating; but the Arkansas quartz which we next tried was not affected by heat, and for work with neutral-salt solutions up to  $306^{\circ}$ , to which we have as yet confined ourselves, it leaves nothing to be desired. Since the thermal coefficient of expansion is so different in the directions parallel to and perpendicular to the main axis of the crystal, it seemed safer to make the axis of the cup parallel to the main axis of the crystal, and this was done.

The process employed for making the quartz cup is as follows: A crystal is selected which is perfectly clear and free from imperfections. A slice, in thickness a little greater than the height of the finished cup, is then sawed out at right angles to the main axis. For this operation a thin tinned-iron disk, whose edge is charged with diamond powder, is rotated in the lathe; and the piece, supported on a sawing table, is pressed lightly against the saw by hand, a wet sponge being held against the edge of the saw with the other hand. This operation of sawing is discussed at some length by Threlfall.<sup>†</sup> It is both easy and rapid if the saw is in good condition. Care must be taken in this and

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\* Phys. Rev., 11, 129-154 (1900).

† On Laboratory Arts, pp. 187-189.

the subsequent operations that the work is not crowded too hard against the abrading surface, as this causes a local rise of temperature which may crack the crystal. A hollow drill, whose internal diameter is but little greater than the external diameter of the finished cup, is then run through the crystal piece at right angles to the sawed surfaces. Such a drill consists merely of a tinned-iron tube provided with a slit running lengthwise, and mounted so that it can be rotated in the lathe. The outer end of the tube is turned off square and is then charged with diamond powder. A small piece of wet sponge is then placed in the tube. Powdered carborundum can be used in place of diamond, and, although it is somewhat slower in starting, it appears to be equally satisfactory afterwards. The core is then taken from the drill and the ends of the cylinder are ground down flat; for the saw has left them somewhat irregular. This operation of grinding is conveniently carried out by means of a carborundum wheel rotated in the lathe, the wheel being kept wet by holding a sponge against it. Before grinding either surface, its bounding edges must be ground off (bevelled); otherwise the edges will break out irregularly. To cup out the cylinder, a hollow drill, whose external diameter is but little less than the internal diameter of the finished cup, is then run into one end to a depth almost equal to that of the desired cavity. The core which is left from this drill is too strong to be broken out without danger of injuring the outside of the cup; so another, smaller one is next run in to the same depth as the first and concentrically with it. This leaves two fragile pieces, a small rod and a thin tube, which are easily broken out. The cup is next mounted so that it can be rotated in the lathe. This is best accomplished by fastening it with stick shellac to the end of a brass rod held in the lathe chuck. To hold firmly, the crystal must be heated above the melting-point of the shellac; this can be done safely by flashing it with a gas flame. The inside of the cup is then ground to its final diameter and the bottom made flat by using carborundum powder upon the end of a brass rod which is a little less in diameter than the cavity and whose end is squared off, the rod being best held in the hand. The small hole is drilled through the bottom of the cup by the aid of a small diamond set in the end of a steel or brass rod. The diamond must, of course, be a little larger than the rod to give clearance for the latter. To start the hole the T-rest is used, but afterwards the rod is supported only by the hand. The tool must be withdrawn and moistened very frequently. The hole may be run halfway through from either end. It is afterwards expanded to its proper size by the aid of a small brass or steel rod and some carborundum powder.

dum. To turn the little V-shaped ridges on the ends of the cup, a diamond is set in the end of a steel rod just as for the boring tool, except that here a larger rod may be used to advantage. The tool is held in the hand and supported on the T-rest just as the ordinary hand tool is used on metal. The outside of the cup is first turned true with the diamond, and the ridges are ground out by holding a flat piece of carborundum (the face of a carborundum wheel answers nicely) against it as it revolves. To support the cup while work is being done on the lower end it is best to fasten in the chuck a piece of brass rod somewhat smaller than the internal diameter of the cup, square off its end, turn a little groove in it which will correspond to the ridge at the bottom of the cup, and then shellac the cup on, so that the ridge comes in the groove. This mode of support ensures getting the ridges, as they should be, in parallel planes and centrally located with reference to the axis of the cup. The operation of polishing is best carried out by means of different grades of corundum powder, using finally oxide of tin. These are applied wet on the end of a soft piece of wood.

In making such a cup an ordinary mechanician, after a little practice on the different operations, will spend perhaps twelve or fifteen hours.

In this connection it may be mentioned that some ready formed cups, made of fused silica, have lately been furnished us by Siebert & Kühn of Cassel, Germany. All that remains to be done to these cups is to drill the small hole in the bottom and turn the ends. They have not yet been tried, but unless they are more acted upon by hot water than those of quartz-crystal, which seems unlikely, they will be preferable for several reasons. For, in the first place, the making of such a cup from crystal is a somewhat tedious operation, and, in the second place, a very rapid cooling of the bomb has to be avoided, as the crystal would otherwise crack. Even with the fused-silica cups it will doubtless be necessary to cool the bomb slowly to avoid loosening the joint, but the cup would not be lost even if the bomb happened to be cooled suddenly. Another advantage of the fused silica is that, owing to its small expansion coefficient, there would be a much smaller change in the cell constant with the temperature (see Section VIII).

The thickness of the brass compensating washer (Z, Fig. 1) can be calculated from the known coefficients of expansion of the quartz-crystal and of the brass and steel used. That used in our bomb was 5.1 mm. in thickness. Of the two gold washers the upper one is made to fit tightly on the electrode rod, while the hole in the lower one is made to correspond with that in the bottom of the bomb. To keep the lower

gold washer from touching the electrode rod, and to keep the latter from touching the steel shell, the following device was employed: The middle part of the steel rod is made about 0.5 mm. smaller in diameter than the hole in the crystal. Three thin strips of mica, each about 2 cm. long and 2 mm. wide, are inserted in the space left between the electrode rod and the crystal, so that the ends of these mica pieces project perhaps 1 cm. below the cup. The mica strips are cut so wide that they have to be pushed into place. They serve to hold the rod in the crystal and keep the lower gold washer in place. The cup can now be grasped by its edge with a pair of tweezers and the electrode rod pushed through the hole in the bottom of the bomb. It is then bolted down. It is next tested to make sure that there is no short circuit between the electrode and the bomb; and finally, to make sure that the joint is tight, the bomb is connected once more to the pump.

If, after the bomb has been in use for some time, it is necessary to remove the lower electrode, it may be done in the following way: The nut, N, cannot be unscrewed, but enough of it can be removed with saw and file so that the remainder will slip through the hole in the brass washer. A light direct blow with the hammer on the end of the electrode rod is then always sufficient to start it out. The brass remaining in the threads of the electrode rod is easily removed with any pointed tool, and the electrode is ready to use again.

The cover, B, is made slightly concave to allow the air bubbles, which might otherwise collect under it, to escape into the electrode chamber above. To line the cover a round disk of platinum-iridium alloy containing 15 per cent iridium is taken, and the two tubes, T<sub>1</sub> and T<sub>2</sub>, are soldered to this with pure gold. This alloy is used rather than pure platinum on account of its greater hardness, which prevents the gold ring from cutting into it.

In the development of the bomb, the tube T<sub>2</sub> has probably caused more trouble than any other part. This is due in part to the fact that at high temperatures the pressure is sufficient to force water through the lining at any unsupported spot. If the tube was made of heavy metal, and especially when it was made of the 2 per cent alloy, it was itself capable, owing to its small diameter, of withstanding the pressure without expanding enough to come into perfect contact with the steel at all points; as a result, the bomb would leak at such points. Or, owing to the greater difficulty in mechanically expanding the small tube to meet the shell, the fit would be so poor at the start that the hydraulic pressure would tear it. Our earlier work here was done with the 2 per cent

alloy before we fully realized the great difference in ductility between this and pure platinum. Because of its extreme ductility gold was then tried. This worked beautifully at first, but finally failed because the 22-carat gold solder employed in making the tube disintegrated under the action of the hot water. Recourse was then had to pure platinum, which completely solved the difficulty. The platinum tube is first expanded by driving in some plugs of cotton with the help of a hammer and a brass rod almost as large as the inside of the tube. Seamless tubing might be advantageously used here, but we used a tube made of sheet platinum soldered with pure gold, and this proved to be entirely satisfactory.

The small tube,  $T_1$ , is conveniently made by rolling up tightly some thin sheet platinum and then flowing gold in to fill the spaces between the convolutions. This gold is fed in from the outside, while the whole tube is kept hot in a large blast-lamp flame. Care must be taken not to use too much gold; otherwise a drop may form inside the tube, and its removal by drilling is extremely difficult. Owing to capillary forces, no gold will go to the space inside until the smaller spaces between the convolutions are all filled, so that there is no danger so long as too much gold is not employed. In this, as in all other operations when gold is used in soldering platinum, the piece should be kept hot no longer than is absolutely necessary, because the gold rapidly alloys with the platinum, and the resulting alloy is more crystalline in structure than either of the constituents and has not their ductility. To make the joint between  $T_1$  and the lining of the cover stronger, the tube is reinforced above this point, as shown by the drawing. This was necessary in our earlier apparatus before the lining was screwed down to the cover, but is probably not necessary in the later form.

As the upper end of the tube  $T_1$  is to act as a valve seat, and as therefore there will be a good deal of downward pressure at this point, the tube has to be well expanded into the conical cavity in the steel at V (Fig. 1). Because of this, and of the further fact that the valve seat should be as soft as possible, it is better to make the upper end of  $T_1$  of solid gold, boring it out later. This is done as follows: The tube is first packed full of asbestos, to prevent gold from getting into it. A band of thin platinum foil is next wound tightly around the upper end and bound on by means of a platinum wire. This band is then pushed partly off of the end of the tube, so as to make a small projecting tube; and pure gold is melted into this until it is full. The platinum foil on the outside of the gold is now filed off. Both tubes are now attached to the cover lining and inserted in place in the cover. Holding the lower

end of  $T_1$  on an anvil, the soft gold, projecting perhaps 3 mm. above the steel at  $V$ , is compressed with a riveting hammer. The asbestos is now drawn out of the tube, and a hole is drilled down through the gold to meet the hole in the platinum.

The valve seat at the start is of the form shown in Fig. 1, and the slightest pressure on the steel bicycle-ball serves to force the ball down into the soft gold tube enough to make the joint tight. But after this process has been repeated a few times the bearing surface of the ball on the gold becomes so large that the pressure which can be obtained by tightening the screw,  $K$ , with the fingers is not sufficient to make the joint tight. The valve seat can be easily brought back to its original condition, however, by filling the depression, which the ball has made, with soft dental gold and opening the hole again with a scratch awl or a drill. The filling is most conveniently accomplished with a little "moss fibre" gold, using the regular dental tool. Of course the top should always be left concave, so that the ball will of itself roll to the center. Time is saved in the end by putting the valve seat in order each time; for, if this is done, there will never be a leak at this point. It is also better to use a fresh steel ball each time. The screw,  $K$ , should fit well, but still turn easily with the fingers; for, if there were much friction here, it would be impossible to tell how much of the force employed in screwing it down was being communicated to the ball and how much was wasted in friction in the screw. Smearing a little vaseline on the screw prevents air from leaking in while the bomb is being evacuated.

The edge of the lining is fastened to the cover by eight steel screws, in the same way as the flange of the lining of the body of the bomb is secured, the only difference being that it is not necessary at the top to recess the edge of the platinum. Care must, of course, be taken that the screws in the top do not come opposite those in the lower part when the top is put on. Two reference marks enable the experimenter to bring the cover always into the same position with respect to the bottom.

The cover lining is forced into place and tested, just as was the lining of the lower part of the bomb, by means of the Cailletet pump, making

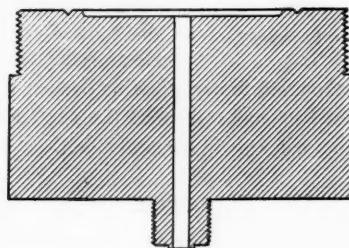


FIGURE 6.

the pump connection with a metal piece like that shown in Fig. 6, which takes the place of the lower part of the bomb.

The construction of the auxiliary electrode is similar to that of the lower one: it will be evident from Fig. 7. The part, *a*, has to be made just as small as is consistent with making the joint tight on the end of the crystal. The platinum covering consists of a little platinum box similar to that used on the lower electrode, a short piece of tubing, *b*, and a piece of platinum wire, *c*.



FIGURE 7.

The gold packing rings are made as follows: A piece of gold wire about 3 mm. shorter than the circumference of the finished ring is cut off, the ends filed square and then soldered together with coin gold. The wire is then annealed and placed on a cast-iron spreader. By pushing a tapered brass plug into this spreader, it is expanded and the ring stretched. By placing a reference mark on the tapered plug, the ring can be stretched to just the same size every time. It, of course, comes off perfectly round, and after annealing is ready for use. Each ring is used but once; but after a number have been used they are remelted and made into fresh wire.

The total weight of platinum used in our bomb is about 185 grams. This, together with the fine construction work involved, makes the initial cost considerable, but the platinum, of course, retains the larger part of its value.

Before adopting the sheet-platinum lining, attempts were made to produce a satisfactory platinum plate on the inner surface of the bomb by the electrolytic process described by Langbein\*; but although a firmly adhering deposit was obtained, it was found not to be dense enough to protect the surface beneath from attack and the liquid from consequent contamination.

#### IV. PROCEDURE FOR THE CONDUCTIVITY MEASUREMENTS.

In making a set of conductivity determinations, the valve seat at the top of the tube  $T_1$  (Fig. 1) is first put in order by putting in a gold filling, as has already been described in Section III. Then any loose

\* Langbein's Electro-Deposition of Metals, 378 (1902).

particles of graphite or dirt adhering to the flange and cover in the neighborhood of the gold packing ring are removed with absorbent cotton saturated with benzene, and the screw thread on the lower part is cleaned in the same manner. Both the upper and lower parts are now rinsed thoroughly with good water, using the fine stream from a wash bottle to remove more effectually any loose particles of graphite which may have got into the bomb upon previously opening it. By this means, too, water can be forced through the fine tube  $T_1$ . If the solution to be investigated is a dilute one, the rinsing must be very thorough. Finally, the bomb is rinsed out with some of the solution, and as much as possible of this is then shaken out. The bomb is then ready for use.

Suppose now it is desired to make a series of measurements at the temperatures up to  $281^\circ$ . An amount of solution which will almost, but not quite, fill the bomb at this temperature is measured in from a pipette previously graduated to contain this amount, as will be described in Section V. A gold packing ring is annealed and cleaned by heating it in the flame of a burner, and it is placed in the groove. The cover is then put in place, taking care not to disturb the ring. The thread in the large nut is next washed out with benzene, to get rid of any solid substance which may have condensed there in a previous heating. With a piece of cloth or absorbent cotton, a lot of finely powdered graphite is then rubbed into the thread and onto the surface which bears on the brass compensating washer. The nut is now screwed on by hand, care being taken not to disturb the cover; otherwise it might be raised slightly, so that particles of graphite would enter the bomb. The apparatus is next transported carefully to the large wrench, and the nut is tightened up. The air pressure is then reduced to about 2 cm. by connecting the small tube with a Richards water pump, the valve is screwed down, the lead-wires bolted on, and the bomb is ready for the measurements.

The conductivity is first measured at  $26^\circ$ . To hasten the equalization of the temperatures, the cold bomb was usually introduced after bringing the bath to about  $30^\circ$ . The other vapor baths are heated up meanwhile.

The bomb is then immersed in the  $140^\circ$  bath, whereupon the conductivity increases very rapidly. The minimum in the telephone is at first greatly disturbed by the boiling of the solution, which takes place strongly at the lower electrode, owing to the fact that this is at the start, because of its position, the hottest part of the bomb. But as the temperature of the solution approaches that of the bath the disturbance decreases, and finally ceases altogether. When the temperature has become almost con-

stant, which is indicated by the constancy of the conductivity, the bomb is removed from the bath, shaken, and returned as quickly as possible. To shake it while hot, a piece of asbestos cloth, with a piece of woollen cloth outside, is used. If the shaking is omitted, the measured conductivity may be too high by as much as 0.5 per cent. This was found to be due to the following facts: At 140° there is still a considerable vapor space left in the bomb, the entire cover being above the liquid surface. During the first part of the heating the xylene vapor is condensed so rapidly by the bomb that it extends up only for a little distance above the bottom of the bomb, leaving the upper part completely out of it. This causes an evaporation of pure water and a condensation of it all over the colder cover, leaving the solution too concentrated. If the bomb is shaken after reaching the temperature of the bath and quickly returned, the same action does not repeat itself, since the top is now as hot as the bottom. The bridge readings are now continued (usually for about thirty minutes) till one perfectly constant for ten to fifteen minutes is obtained.

The bomb is then transferred to the naphthalene bath. Shaking was found to have no effect at this temperature, owing, doubtless, to the fact that the liquid level has then risen almost to the cover, so that large drops cannot adhere to the latter, and to the fact that the surface tension has diminished, so that less water is held clinging to the walls of the narrow chamber in the cover.

The bomb is next brought into the 281° bath. It is now necessary to keep constant watch of the conductivity between the upper auxiliary electrode and the walls of the bomb, so as to be sure that too much solution has not been put into the bomb. The reasons for putting in solution enough at the start to so nearly fill the bomb at the highest temperature are first, to reduce the vapor space at all the temperatures as much as possible, since a correction has to be made for the amount of solvent in this space; and secondly, to see that the bomb is absolutely tight even at the highest temperature, when the solution is in contact with the upper electrode. This latter is important, since a leak, if it took place above the liquid level, would cause a loss of pure solvent and a consequent increase in the concentration of the solution.

After completing the measurements at 281°, the bomb is returned to the 218° bath, then to the 140° bath, and finally it is brought back to 26°. In going from a higher temperature to a lower much time is saved by cooling the bomb, in front of a fan outside the bath, to a temperature which is at least as low as that next desired; for while heating in a

vapor bath is rapid, the cooling in it of a hotter body is very slow. During the first half of the experiment, where the bomb is introduced each time into a hotter bath, stirring inside the bomb takes place of itself, it being accomplished by the rising vapor bubbles and the rapid convection currents caused by the bottom of the bomb being so much hotter than the top during the heating. During the second half it is necessary to provide for this by shaking the bomb before putting it into each bath. How much shaking is necessary can be determined by repeating the operation and seeing whether the conductivity has been affected by it.

The advantages derived from cooling the bomb down through the same series of temperatures and again taking measurements are that these furnish a check on the accuracy of the preceding ones, and especially that they show whether or not there has been any contamination, and if so, between what temperatures it took place and to how much it amounts.

The bomb is opened as soon as the experiment is completed, since otherwise there may be trouble in getting the cover off because of the strong adhesion of the gold packing ring to the platinum lining below. This effect increases with use, since a small amount of gold from the ring adheres to the platinum each time, and subsequent rings will adhere more firmly to this gold than they would to a clean platinum surface. The effect can easily be reduced, however, as soon as it grows troublesome, by rubbing the platinum cover, where it comes in contact with the ring, with a burnisher and by marking in the groove with a lead pencil. The trace of graphite which adheres to the surface is very effective.

When the bomb is not in use, good water is left standing in the lower part. The cover is inverted and the upper chamber similarly kept filled with water. If for the next experiment a more dilute solution is to be employed, the bomb must first be heated with good water to perhaps  $218^{\circ}$  for some little time. No amount of rinsing or soaking out at ordinary temperatures will answer the purpose. There is on this account a great saving of time effected by beginning with the dilutest solution to be investigated, and afterwards measuring those more and more concentrated.

Our measurements at  $306^{\circ}$  were carried out, for the most part, after complete experiments up to  $281^{\circ}$  had been made, so that they usually consisted merely of measurements at  $26^{\circ}$ ,  $306^{\circ}$ , and again at  $26^{\circ}$ .

### V. PROCEDURE FOR THE SPECIFIC-VOLUME MEASUREMENTS.

To determine the specific volume of a solution at any temperature, such an amount of solution is weighed into the bomb as will bring the liquid level up onto the auxiliary electrode at that temperature. This amount was determined by successive heatings with increasing volumes of solution.

A pipette of the form represented by Fig. 8 was made for each of the temperatures  $218^{\circ}$ ,  $281^{\circ}$ , and  $306^{\circ}$ . The stem is graduated between *a* and *b*, and the capacity up to these points is roughly determined by weighing. The volume of the pipette is made such that for water or dilute solutions it will deliver the right amount into the bomb when filled up to the point *b*. For more concentrated solutions the expansion is less, so that more of the solution must be used. The graduations on the pipette serve only as an indication of how much solution to take. The exact amount used is obtained by weighing the pipette filled and then again after discharging. During the weighing the tip is covered with a small test tube, *c*, which is held on by the rubber band, *d*.



FIGURE 8. The bomb is first dried out by rinsing it with alcohol and ether. The residue left by the ether upon evaporation is sufficient to affect the conductivity of the diluter solutions employed, so that no attempt was made to determine the conductivity of such solutions at the same time as their specific volume. The solution is boiled to expel the air. This increases the concentration slightly; but this is of no consequence if, as was usually the case, the experiment was made solely to determine the specific volume. If it was also to serve for conductivity measurements, the solution was boiled gently in a tall platinum vessel which was weighed with its contents before and after boiling. This gave the loss of solvent during the operation. Knowing this and the amount of solution originally present in the cylinder, the final concentration is easily calculated. After weighing the solution in from the pipette, the bomb is closed, and the air pressure reduced to 2 cm. Upon heating, careful watch is kept of the readings with the auxiliary electrode to make sure that too much solution has not been put in. After the conductivity of the upper chamber has been constant long enough to show conclusively that the temperature has become stationary and that the bomb is absolutely tight (even the slightest leak being of course indicated by a

constant decrease in the conductivity of the upper chamber), the conductivities between the walls of the bomb and both the upper and lower electrodes are measured carefully, and the temperature of the bath is observed. The experiment is then complete.

The ratio of these two conductivities is calculated, and the corresponding volume is obtained by interpolation from a plot obtained as described in Section VI. This volume, corrected for the expansion of the bomb and then divided by the weight of solution in the bomb, gives the specific volume of that solution at the temperature in question, and this quantity divided by the specific volume of the solution at  $4^{\circ}$  gives the volume of that quantity of the solution that would at  $4^{\circ}$  occupy one cubic centimeter, this quantity being most convenient in subsequent computations.

#### VI. STANDARDIZATION OF THE APPARATUS.

*Thermometers.*—These were calibrated by the method recommended by Crafts,\* first for irregularities of bore and then at the fixed points  $0^{\circ}$ ,  $100^{\circ}$ ,  $218^{\circ}$ , and  $306^{\circ}$ . For the last two temperatures the vapors of boiling naphthalene and of benzophenone were used. These substances were obtained from Kahlbaum, and were purified in the manner suggested by Crafts, until their melting points came within his limits. The form and dimensions of the vapor bath used in establishing the  $218^{\circ}$  and  $306^{\circ}$  points were essentially those given by him. To reduce the temperatures lying between the fixed points to the gas scale, his table of corrections for French glass was also used, our thermometers being of the same make as those used by him. At the beginning every temperature measurement was followed by a lag ice-reading; but this was found to be unnecessary, since the thermometers showed no lag. The ice-reading was, however, taken frequently, to make sure that the zero did not change from another cause,—evaporation of mercury from the bulb below and condensation in the chamber above. This effect was not apparent even after long use at temperatures up to  $280^{\circ}$ ; but above this the zero would fall perhaps  $0.1^{\circ}$  from two or three days' use. When in use at  $306^{\circ}$ , instead of taking an ice-reading the thermometer was first placed in the benzophenone heater and then in the calibrating apparatus containing perfectly pure benzophenone. The difference in reading (usually amounting to  $0.1$ – $0.2^{\circ}$ ) was deducted from the true boiling-point of benzophenone at the observed barometric pressure.

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\* Am. Chem. Jour., 5, 307–338 (1883–84).

Two thermometers were calibrated in this way, and in actual use their corrected readings were always found to agree satisfactorily with each other.

*Slide-Wire Bridge and Resistance Coils.*—The slide wire was calibrated by the method of Strouhal and Barus.\* The resistance coils were calibrated by comparison with a standard bridge of this Institute.

*The Cell-Constant.*—In order to reduce the observed to specific conductivities, the "cell-constant" was determined in the usual manner, by measuring in the bomb solutions of known conductivity. For this purpose the measurements at 26° of the solutions of both potassium and sodium chlorides, which were afterward studied at higher temperatures, were employed, the mean of the most reliable of them being taken. (See Section XI.)

*The Volume of the Solution in the Bomb and the Corresponding Cell-Constant Ratio.*—It was stated above that the volume of the solution at any time in the bomb was determined by measuring the ratio of the conductivities between the walls of the bomb and the lower and upper electrodes respectively. This ratio will hereafter be called the cell-constant ratio. Its value is, of course, independent of the nature of the solution in the bomb, and is determined fully by its height in the narrow chamber, and therefore by its volume. To find the values corresponding to different volumes, we proceeded as follows: The bomb is first dried by rinsing it with alcohol and ether. Some 0.02 molar potassium chloride solution † is then boiled to free it from air, and right after cooling, enough of this to fill the bottom part of the bomb to within 1-2 mm. of the flange is weighed in from a pipette. The mouth of the pipette is kept under the surface to diminish the absorption of air. The cover is next put on and screwed down, care being taken not to tip the bomb enough to get any of the solution up onto the mouth of the tube  $T_1$ . By means of the water pump the air pressure in the bomb is reduced to about 2 cm., and the valve is then closed. If the air is not removed from the solution at the start, it comes out rapidly upon reducing the pressure and spatters some of the solution up into the tube  $T_1$ , thus allowing it to be swept out by the air current.

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\* Wied. Ann., 10, 826 (1880). See also Kohlrausch and Holborn, Leitvermögen der Elektrolyte, 45 (1898).

† The reasons for taking this solution instead of pure water are that it makes the conductivity at the upper electrode high enough to give a good minimum, and that the solution is so strong that contamination could not possibly make any trouble.

The lead wires are now bolted on and the bomb is placed in the liquid xylene bath, serving ordinarily for the 26° measurements, and the temperature of the latter is raised by means of the heating coil. The liquid level in the bomb is at the start about 3 mm. below the point of the auxiliary electrode, so that the resistance of the upper cell is shown by the conductivity apparatus to be infinite; but upon heating, the level rises and finally touches the electrode, whereupon the resistance suddenly sinks to perhaps 1000 ohms. The temperature of the bath (perhaps about 130°) is now held constant until the solution in the bomb has also attained it, as will be indicated by the resistance of the lower and, far more sensitively, by that of the upper cell becoming constant. Both these resistances are then noted, and the temperature is measured.

The temperature is now raised by steps of three or four degrees until that ratio of the cell constants is reached which corresponds to the bomb being almost completely full. This limiting ratio can be determined cold at any time by measuring the resistance of the lower cell and then inverting the bomb and measuring that of the upper cell. Finally, the cell-constant ratios are plotted as abscissae and the corresponding volumes as ordinates, whereby a straight line is obtained.

The computation of the volumes is made with the help of the following data. Zepernick and Tammann\* have found that equal volumes of a 0.52 normal potassium chloride solution and of water at 0° upon heating from that temperature to 140° become different from each other by only 0.1 per cent. It is therefore perfectly safe to assume that the expansion of the 0.02 normal potassium chloride solution used by us is the same as that of pure water. From Hirn's† results the specific volume of water at the temperature in question, but under a pressure of 14.8 atmospheres, may be obtained. At 135°, the mean temperature of the calibration experiments, the vapor pressure is 3.1 atmospheres. Hirn's result should then be reduced to this pressure. The coefficient of compressibility of water has been investigated by Pagliani and Vicentini‡ up to 100°. Plotting values and extrapolating gives 0.000048 for the coefficient at 135°, or for the fractional decrease in volume per atmosphere pressure. Hirn's value should then be increased by  $0.000048 \times (14.8 - 3.1) \times 100 = 0.056$  per cent. Multiplying the value so

\* *Ztschr. phys. Chem.*, **16**, 665 (1895).

† G. A. Hirn, *Ann. chim. phys.* (4), **10**, 32 (1867). His series of observations covers the range of temperature up to 180°. Between 110° and 143° his values differ from those found by Zepernick and Tammann by only 0.02 per cent.

‡ *Landolt und Börnstein, Tabellen*, 96 (1894).

obtained by the weight of solution employed and by the specific gravity of the cold solution referred to water at the same temperature, the volume corresponding to the observed cell-constant ratio is obtained.

### VII. PREPARATION OF THE SUBSTANCES AND SOLUTIONS.

The sodium chloride used was purified by precipitation with hydrochloric acid gas. It was then washed with hydrochloric acid, dried, and finally ignited until decrepitation ceased.

The potassium chloride was precipitated twice with hydrochloric acid gas, crystallized from hot water, dried, and finally ignited.

Solutions were made up, by weighing out the salts, so as to be almost exactly 0.1 and 0.01 normal at  $4^{\circ}$ . The solutions of smaller concentration were made by diluting the 0.01 normal one with the help of two graduated flasks.

The equivalent weights used are as follows: K = 39.14, Na = 23.05, Cl = 35.46. All weighings were reduced to a vacuum.

The water used throughout this investigation was prepared by redistilling ordinary distilled water, to which alkaline permanganate solution was added, from a steam-jacketed copper still with a tin condenser. The first quarter of the distillate was rejected, and the following portions were condensed hot (between  $60^{\circ}$  and  $90^{\circ}$ ). The water had a specific conductivity of  $(0.7 \text{ to } 1.0) \times 10^{-6}$  reciprocal ohms.

### VIII. DISCUSSION OF THE SYSTEMATIC ERRORS AND THEIR CORRECTION.

*Errors Affecting the Specific-Volume Values.*—1. In calculating the specific-volume, the volume of the bomb was directly determined at about  $135^{\circ}$ , as described in Section VI, and the expansion of the metal from this point to the temperatures of the experiments was corrected for. Andrews,\* working with "soft" cast steel, which corresponds to the material from which the bomb was constructed, found the mean coefficient of cubical expansion between  $100^{\circ}$  and  $300^{\circ}$  to be 0.0000450; and this value was adopted for the corrections. The difference between his steel and that used in the bomb can hardly be great enough to cause an appreciable difference in the coefficient of expansion, since his values for two steels as different as Bessemer steel with 0.15 per cent combined carbon and cast steel with 0.45 per cent differ by only 6 per cent; and an error of even 6 per cent in the coefficient of expansion would produce

\* Proc. Roy. Soc., 43, 299 (1887).

a maximum error, even at 306°, of only 0.05 per cent in the specific volume.

2. The quartz-crystal cup expands upon heating, thus diminishing the volume of the bomb occupied by the solution. The correction for this, even at 306°, amounts to only -0.03 per cent.

3. The bomb expands owing to the pressure within. At 306°, where this correction is greatest, the vapor pressure plus the air pressure may be estimated at 100 atmospheres. Assuming that the modulus of elasticity of the steel is 17372 kgm. per sqmm., which is the value found by Pisato\* at 300°, the volume correction due to this cause is +0.025 per cent. This is opposite in sign and essentially equal to the preceding correction: they therefore eliminate each other.

4. The volume of the tube  $T_1$  is only 0.07 ccm. or 0.06 per cent of the whole volume of the bomb. It is therefore so small that no irregularities in the extent to which it is filled with solution could much affect the result.

5. The volume of the bomb depends somewhat on the extent to which the large nut is tightened up and the gold packing-ring compressed. Four of the gold rings which had been used were chosen at random, and the mean thickness of each was calculated from measurements made at eight equidistant points with a micrometer caliper. The average deviation from the mean thickness of these rings was such as to affect the volume of the bomb by only 0.02 per cent. So this source of error can be unhesitatingly disregarded, especially as each final specific-volume value is the mean of the values obtained from several independent runs.

6. The bomb is never completely filled with liquid, the vapor space amounting, on an average, to about 1 ccm. or 0.8 per cent of the total volume of the bomb (about 124 ccm.). A certain fraction of the water is therefore vaporized, and the specific volume appears too small by a corresponding amount. The specific volume of the vapor is not yet known above 200°. By extrapolation, however, from the values up to 200°, the specific volume of the vapor at 218° is found to be seventy-five times that of the liquid. From this it follows that at 218° the correction is only  $\frac{1}{24} \times \frac{1}{75}$ , or about 0.01 per cent.

Such a calculation is not possible at the higher temperatures, 281° and 306°; but that no considerable error arises from this source was shown by direct experiments. Namely, when two or more specific-volume determinations were made, the amount of solution taken in the different experiments was purposely varied, so that the vapor space should

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\* Nuovo Cimento (3), 4, 152 (1878).

vary from about 1.8 ccm. to 1 ccm. If, now, a considerable amount of the water were present in the vapor space, the specific-volume values obtained would, of course, be larger the smaller that space. As a matter of fact, however, the values obtained with the 1 ccm. vapor space were as often smaller as they were larger than those obtained with the 1.8 ccm. vapor space. In other words, no difference greater than the variable experimental error was observed. The error due to this source is therefore probably less than 0.1 per cent.

7. The temperature measurements may be regarded as accurate to within  $0.2^{\circ}$ ; and this of itself introduces an uncertainty of only 0.07 per cent in the worst case, that of the  $306^{\circ}$  values. That the bomb and its contents actually attained the temperature of the surrounding vapor is shown by the fact that the extremely sensitive reading of the upper electrode remained constant indefinitely after it had once become so; and by the fact that there could not be a continuous loss of heat of appreciable magnitude from the bomb to the surroundings, since upon the sides the bomb was protected against radiation and cold convection-currents by the iron shield with the vapor outside, and since above there was always a layer of vapor 10 cm. in height, and since the dropping back of condensed liquid on to the bomb was prevented by the mica shield; moreover, the copper lead-wires were only 1.2 mm. in diameter and passed through the upper layer of vapor before emerging.

8. Another possible source of error might be the gathering of vapor bubbles on the under surface of the cover, whereby the apparent volume of the liquid would be increased. That this did not occur was shown by removing the bomb from the heater, shaking vigorously, immediately replacing it, and taking conductivity readings as soon as the temperature had again become constant, whereby the same readings were obtained as before the shaking.

9. The air was not entirely removed from the bomb at the start, and, as the solution expands and the temperature rises, the air pressure increases. Assuming that the preliminary boiling had removed all of the air from the solution in the beginning, and that there is no solubility of the air in the liquid at the high temperatures, its pressure can be calculated by the gas laws. At the temperatures of 218, 281, and  $306^{\circ}$ , it would thus amount to about 1, 2, and 2.5 atmospheres respectively. The effect of these air pressures on the specific-volume values cannot be calculated, since the compressibility at these temperatures is not known; but for these small pressures it is undoubtedly less than the errors of observation.

10. If the vapor above the solution had an appreciable conductivity it would make the conductivity between the upper electrode and the bomb appear too great. But this is not the case, as is shown by the fact that unless the liquid is in contact with the electrode there is no measurable conductivity here, even at 306° with a 0.1 normal KCl solution. We can at present only assign an upper limit to the conductivity of the vapor: but it certainly does not exceed  $\frac{1}{200000}$  part of that of the solution.

*Errors Affecting the Conductivity Values.*—1. All the errors in the values of the specific-volume have an effect of the same magnitude upon those of the equivalent conductivity, with the important exception of that due to the amount of solvent in the vapor space at the two highest temperatures, 281° and 306°. No error arises from this last source by reason of the fact that, owing to the increase in concentration of the solution, the specific conductivity increases in the same proportion as the volume diminishes; for at 281° and 306° (but not at 140° and 218°), the quantity of liquid in the bomb was the same in the two series of measurements.

2. The cell-constant might be expected to vary with the height of the liquid level in the bomb; but direct experiment showed that for the range of the liquid level in our measurements the effect of this was less than the error of observation. The smallest amount of solution employed in any of the experiments was first introduced into the bomb and the conductivity measured at 26°. Then more of the same solution was introduced until the liquid was in contact with the whole cover; but the resistance was not measurably changed.

3. The cell-constant changes with the temperature owing to two causes: first, the expansion of the quartz-crystal cup; and, secondly, that of the bomb itself. The correction for this is calculated as follows: The resistance inside the bomb may be considered as made up of two parts, that (*a*) inside the crystal cup, and that (*b*) between the mouth of the cup and the platinum lining. The ratio of *a* to *b* can be roughly determined by putting any solution into the bomb, measuring the resistance, and then introducing a third electrode in the form of a platinum disk placed over the mouth of the cup, and measuring the resistance between this new electrode and the electrode at the bottom of the cup. This ratio, so determined, is not strictly identical with the actual one, since the lines of current-flow inside the quartz cup have been somewhat changed in direction by the interposition of the new electrode; but for the present purpose the approximation suffices. The ratio  $\frac{a}{a+b}$

was thus found for Cell II to be  $\frac{a}{a+b}$ . Le Chatelier \* has studied the expansion of quartz both parallel and at right angles to the main axis up to  $1000^\circ$ ; and, with the help of his values, the resistance of one of the cups was calculated to decrease by 0.69 per cent of its value upon heating from  $26^\circ$  to  $306^\circ$ . Multiplying this by  $\frac{a}{a+b}$  gives 0.53 per cent for the decrease in the resistance of the bomb due to the expansion of the cup. On the other hand,  $b$  will increase at a rate roughly proportional to the linear expansion of the bomb, or between  $26^\circ$  and  $306^\circ$  by  $0.000015 \times (306 - 26)$ , or 0.42 per cent. Multiplying this by  $\frac{b}{a+b}$  gives 0.10 per cent for the increase in resistance of the bomb due to the expansion of the shell. The total decrease in the resistance of the bomb is therefore 0.43 per cent. The change in the cell-constant is similarly calculated for the other temperatures. These corrections are given in Table IV and have always been applied to the results.

4. The effect of the pressure on the cell-constant is entirely negligible. For at  $306^\circ$  the radius is increased by the pressure 0.01 per cent, and this affects the cell-constant by only 0.002 per cent.

5. The resistance of the lead-wires has to be deducted from the measured resistance of the bomb; and since a portion of the leads is subjected to the temperature of the bath, this correction is different for different temperatures. This resistance may be considered as made up of three parts:  $R_1$ , the constant resistance of the heavy leads;  $R_2$ , the resistance of the small leading-in wires,  $L_1$  and  $L_2$ ; and  $R_3$ , that of the steel electrode rod.  $R_1$  and  $R_2$  were measured at room temperature. For the other temperatures  $R_2$  was calculated from its value at room temperature.  $R_3$  was calculated from its dimensions and the specific resistance of steel. The maximum value (at  $306^\circ$ ) of the total resistance of the lead-wires was 0.061 ohms.

6. In the case of the more dilute solutions it was necessary to correct for the conductivity of the water used. To do this, some water prepared in the same way and of the same conductivity cold as that used for making up the solutions was put into the bomb, and just such a set of experiments was made with it as had been made with the solutions. Then for any temperature the conductivity of the water, measured at that same temperature and under the same conditions, was deducted

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\* Compt. rend., 108, 1046 (1889).

from that of the solution. This at the same time corrects for contamination, since, with a dilute, neutral-salt solution, there is no apparent reason why the contamination should not be the same as for water. For the dilutest solution used, 0.0005 normal, the maximum correction (at 306°) amounts to 1.9 per cent. See also Section XI.

7. In the conductivity experiments, the vapor space at 140° and 218° was considerable, so that at these temperatures a correction has to be applied for the vaporized solvent, since the solution is more concentrated than it would otherwise be. This correction was calculated from the known volume of the vapor in the bomb and its specific volume, using for the latter the data of Zeuner\* which go up to 200°, and extrapolating for the 218° value. The correction amounts to +0.05 per cent at 140° and +0.18 per cent at 218°. As explained above, it is not required in the case of the 281° and 306° values.

8. The temperature measurement at 26° is certainly more accurate than the work requires. Above this, the temperature reading is probably correct to 0.2°. Most of the uncertainty in the equivalent conductivity values introduced by this possible error finds expression in the specific-volume values, and this has already been considered. Besides this there is the much smaller effect on the observed resistance of the bomb. The total uncertainty in the equivalent conductivity arises from both these sources: that due to 0.2° is in the worst case (at 218°) 0.09 per cent, and where, as has usually been the case, several experiments are made and the mean taken, this effect tends to be eliminated.

#### IX. EXPERIMENTAL DATA RELATING TO THE SPECIFIC-VOLUME DETERMINATIONS.

All of the measurements have been included in Table I, with the exception of two, which, though agreeing well with the others, were known to be less reliable.

The first and second columns are self-explanatory.

The third column gives the concentration of the solution at 4°, expressed in equivalents per liter.

The fourth column gives the corrected temperature of the experiment.

The fifth column gives the number of grams of solution which were weighed into the dry bomb at the start.

The sixth column gives the volume expressed in cubic centimeters, which, at the temperature (135°) at which the bomb was calibrated, corre-

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\* Landolt und Börnstein, Tabellen, 63 (1894).

TABLE I.  
THE SPECIFIC-VOLUME DATA.

Date.	Salt.	Equiva- lents per Liter.	Temper- ature.	Weight of Solution.	Volume Uncor- rected.	Specific Volume.	Sp. Vol. Ratio, $218^{\circ}/4^{\circ}$ .
Mar. 31, 1902	NaCl	0.002	216.8	104.16	122.75	1.1831	1.1851
Apr. 2, 1902	"	"	217.2	104.58	123.58	1.1863	1.1878
Apr. 3, 1902	"	"	217.9	103.44	122.18	1.1859	1.1861
						Mean . . .	1.1863
May 2, 1902	NaCl	0.1	218.0	103.52	121.79	1.1862	1.1862
							$281^{\circ}/4^{\circ}$ .
Apr. 14, 1902	NaCl	0.002	281.0	92.11	122.08	1.3343	1.3343
Apr. 14, 1902	"	"	281.1	92.97	123.51	1.3374	1.3372
Apr. 18, 1902	"	"	281.1	92.65	122.94	1.3359	1.3356
						Mean . . .	1.3357
Apr. 29, 1902	NaCl	0.1	281.2	92.83	122.07	1.3237	1.3287
May 1, 1902	"	"	280.7	93.27	122.37	1.3207	1.3275
June 10, 1902	"	"	281.8	93.34	122.85	1.3248	1.3272
						Mean . . .	1.3278
							$306^{\circ}/4^{\circ}$ .
Mar. 11, 1903	NaCl	0.002	306.3	85.40	121.82	1.4373	1.4360
Mar. 27, 1903	"	"	305.8	85.35	121.30	1.4318	1.4327
						Mean . . .	1.4343
Feb. 20, 1903	NaCl	0.01	306.7	85.69	122.14	1.4362	1.4337
Jan. 17, 1903	NaCl	0.1	305.2	86.89	120.94	1.4106	1.4201
Mar. 31, 1903	"	"	305.2	87.01	121.92	1.4117	1.4212
						Mean . . .	1.4207
Feb. 17, 1903	KCl	0.01	304.7	85.61	121.24	1.4270	1.4335
Feb. 18, 1903	"	"	306.0	85.76	122.01	1.4335	1.4342
						Mean . . .	1.4338
Jan. 30, 1903	KCl	0.1	304.9	86.75	121.56	1.4119	1.4233
Feb. 10, 1903	"	"	306.3	86.78	122.05	1.4171	1.4223
Feb. 16, 1903	"	"	305.3	86.41	121.29	1.4143	1.4239
*Feb. 16, 1903	"	"	305.3	86.41	121.24	1.4137	1.4233
						Mean . . .	1.4232

\* Same solution as in preceding experiment, after cooling, shaking, and reheating.

sponds to the observed cell-constant ratio. This volume was obtained by interpolation from a plot made as described in Section VI. The actual volume occupied by the solution at the higher temperature is greater than this by an amount equal to the expansion of the bomb upon heating from  $135^{\circ}$  to that temperature. As there stated, the temperature-coefficient of volume expansion of the steel shell of the bomb is assumed to be 0.000045 per degree.

The seventh column gives the specific volume of the solution at the temperature of observation. It is obtained by dividing the values of the preceding column, after correcting them for the expansion of the bomb as just described, by the weight of solution given in the fifth column.

The last column gives the ratio of the specific volume at the round temperatures  $218^{\circ}$ ,  $281^{\circ}$ , and  $306^{\circ}$ , to that of the same solution at  $4^{\circ}$ . Thus, this ratio shows the volume occupied by that quantity of solution which at  $4^{\circ}$  has a volume of 1 ccm. The values are obtained from those of the preceding column by reducing them to these temperatures by means of the temperature-coefficient obtained from our specific-volume values, and then dividing the results by the specific volumes of the solutions at  $4^{\circ}$ . These specific volumes are as follows: 0.9958 for 0.1 normal, and 0.9996 for 0.01 normal sodium chloride; and 0.9954 for 0.1 normal, and 0.9995 for 0.01 normal potassium chloride.\*

#### X. THE RESULTS OF THE SPECIFIC-VOLUME DETERMINATIONS.

The final results are brought together in the following table. The value at  $140^{\circ}$  is that found by Hirn † for pure water reduced from the higher pressure which he employed to the vapor-pressure.

The results with the 0.002 normal solution may be regarded as completely identical with those that would be obtained with pure water; for this solution contains only about 0.01 per cent of salt; and, moreover, the experiments themselves show that there is no difference between the specific-volume ratio of the 0.002 and 0.01 normal solutions, and that the difference between the latter and that of the 0.1 normal solution is somewhat less than one per cent, which indicates that the order of magnitude of the difference between pure water and the 0.002 normal solution is

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\* These values were computed from the densities given by Kohlrausch and Hallwachs (Wied. Ann., 50, 122, 1893) for NaCl at  $18^{\circ}$ , and from that given by Kohlrausch (Leitvermögen der Elektrolyte, 76) for a normal KCl solution at  $18^{\circ}$ , under the assumptions that the change in density is proportional to the concentration and that the expansion is the same between  $4^{\circ}$  and  $18^{\circ}$  for these solutions as for water.

† Hirn, Ann. chim. phys. (4) 10, 32 (1867).

TABLE II.

RATIO OF THE SPECIFIC VOLUME AT VARIOUS TEMPERATURES TO THAT AT 4°.

Substance.	Equivalent Concentration at 4°.	Specific-Volume Ratio.				
		26°.	140°.	218°.	281°.	306°.
NaCl	0.002	1.0032	1.0803	1.1862	1.3357	1.4343
"	0.01	"	"	....	....	1.4337
"	0.1	"	"	1.1861	1.3278	1.4207
KCl	0.01	"	"	....	....	1.4338
"	0.1	"	"	....	....	1.4232

0.02 per cent. The specific volume of water is therefore 1.186 at 218°, 1.336 at 281°, and 1.434 at 306°. It is, according to our estimate of the possible errors, almost certain that these values are not in error by as much as 0.3 per cent, and it is probable that the error does not exceed half this amount. Previous determinations\* of the specific volume of any considerable degree of accuracy have extended only up to 180°.

Attention may also be called to the facts that the 0.1 normal solutions between 218° and 306° expand appreciably (0.8 — 1.0 per cent) less than pure water, but that the difference (0.2 per cent) between the solutions of the two salts scarcely exceeds the experimental error.

## XI. EXPERIMENTAL DATA RELATING TO THE CONDUCTIVITY DETERMINATIONS.

*The Cell-Constant.* — This was calculated from the conductivity measurements at 26°, using for the specific conductivities of the 0.1 and 0.01 normal potassium chloride solutions the standard values of Kohlrausch, Holborn, and Diesselhorst,† and for the other solutions the values at 18° of Kohlrausch and Maltby,‡ and the temperature-coefficients of Déguisne.§ The quartz-crystal cup which was used for the first half of

\* Hirn, loc. cit. Waterston (Phil. Mag. (4) **26**, 116–134, 1863) has, to be sure, made rough measurements from 210 to 320°; but this was done in a glass apparatus which was greatly attacked.

† Wied. Ann., **64**, 440 and 451 (1808).

‡ Wissenschaftl. Abhandlungen phys.-techn. Reichsanstalt, **3**, 210 (1900).

§ Dissertation, Strassburg (1895); Kohlrausch and Holborn, Leitvermögen der Elektrolyte, 190.

the measurements (Cell I) was accidentally broken, and a new one had to be substituted for the rest of the work. After making three experiments with the new cup, the platinum lining of the lower part of the bomb had to be removed and repaired, and this operation changed the cell-constant. The term Cell II<sub>a</sub> will be used to characterize the bomb as it was in these first three experiments with the new cup, and the term Cell II as it was in all subsequent work. With these exceptions, the cell-constant calculated from measurements made at widely different periods did not vary throughout the work. Even when the electrode was removed in case of a leak, and then replaced, it did not make any measurable difference, as was, indeed, to be expected, since the value of the cell-constant is so largely determined by the dimensions of the quartz cup. The values of the cell-constants, with the solutions from which they were derived, are as follows:

TABLE III.

## CELL-CONSTANTS.

Cell I.			Cell II.		
Substance.	Equivalents per liter.	Cell-Constant.	Substance.	Equivalents per liter.	Cell-Constant.
KCl	0.1	0.8294	KCl	0.1	0.9853
NaCl	0.1	0.8288	"	0.01	0.9845
"	0.01	0.8280	"	0.002	0.9850
KCl	0.002	0.8280	NaCl	0.002	0.9840
NaCl	0.002	0.8317	Mean of first two . .		0.9849
Mean of first three . .		0.8287	Cell II <sub>a</sub> .		
			NaCl	0.1	0.9949

The original data from which these were calculated are all given in Table VI. Each cell-constant value is the mean of all of the values calculated from all of the experiments on the solution in question at 26°.

The values derived from the 0.002 normal solutions are not included in the means, because, owing to the higher dilution, they are probably

not so reliable as the others. They are given here, especially to show that our conductivity measurements were not affected either by polarization or by any unsymmetry in the telephone; for had this been the case, our cell-constant values calculated from these solutions would not have agreed with those derived from the 0.1 normal solutions.

As explained in Section VIII, the cell-constant changes with the temperature; the percentage corrections to be applied at the different temperatures of the experiments to the 26° values are given below in the table.

TABLE IV.

## CELL-CONSTANT CORRECTIONS.

	140°.	218°.	281°.	306°.
Cell I	-0.18	-0.22	-0.34	....
Cell II <sub>a</sub> }	....	....	....	-0.43
Cell II }				

*The Water Correction.* — The conductivity of the water used at the various temperatures of the experiments was subtracted from the measured conductivity of the solution. Two experiments, the data of which are given in Table V, served as a basis for the correction. For a fuller discussion of this correction, see Section VIII.

The last column gives the calculated corrections to be applied at the various temperatures to the observed resistances in the case of a 0.002 normal sodium chloride solution. It is given here, especially to show the order of magnitude of these corrections. They were similarly calculated for the other solutions.

*The Conductivity Data.* — The first column in Table VI contains the corrected temperatures, given in the order followed in the experiment.

The second column gives the concentrations, corrected in the case of the 140° and 218° values for the solvent in the vapor space. The correction is made as explained in Section VIII, and amounts to +0.05 per cent at 140° and +0.18 per cent at 218°.

The third column contains the observed resistances of the bomb, expressed in ohms, after correcting for errors in the resistance coils and slide wire, and deducting the resistance of the lead-wires.

The last column gives the equivalent conductivities, obtained by dividing the cell-constant for the given temperature by one one-

TABLE V.

WATER. CELL I. (MAY 14, 1902)		
Temperature.	Resistance.	Correction for 0.002 Normal NaCl Solution.
26	1180000	+0.28%
140	280000	+0.33%
218	163000	+0.41%
282	137000	+0.45%
218	155000	+0.43%
140	220000	+0.42%
26	800000	+0.41%
WATER. CELL II. (FEB. 28, 1903.)		
Temperature.	Resistance.	Correction for 0.002 Normal NaCl Solution.
26	980000	+0.38%
306	140860	+0.53%
26	600000	+0.62%

thousandth part of the concentration (given in the second column) and by the resistance (given in the third column) after correcting this for the water.

## XII. SUMMARY OF THE CONDUCTIVITY VALUES.

All of the equivalent conductivity values of Table VI have been brought together in Table VII, after reducing them by means of the temperature-coefficient obtained from our values, to round temperatures. The different solutions always differed slightly from the round concentrations given in the table, but the difference is too small to affect the equivalent conductivities in the last place given. The first column gives the date of the experiment; the second, the equivalent conductivity "Initial" measured at 140° immediately after the measurements at 26°; and the third, the equivalent conductivity "Final" measured upon returning to 140° after making measurements at the higher temperatures. The following columns for the higher temperatures are similar to the

TABLE VI  
THE CONDUCTIVITY DATA.

NaCl: 0.10275 normal at 4°. — Cell I. (April 29, 1902.)				NaCl: 0.10311 normal at 4°. — Cell I. (April 30, 1902.)			
Temper- ature.	Equivalents per Liter.	Resist- ance.	Equiv. Con- ductivity.	Temper- ature.	Equivalents per Liter.	Resist- ance.	Equiv. Con- ductivity.
25.91	0.10242	74.55	108.54	25.91	0.10278	74.25	108.60
281.2	0.07733	15.823	675.0	138.6	0.09565	21.550	401.6
139.7	0.09520	21.568	403.1	217.8	0.08713	16.217	585.2
217.8	0.08680	16.278	585.2	NaCl: 0.10153 normal at 4°. — Cell I. (May 1, 1902.)			
25.91	0.10242	74.52	108.59	25.91	0.10118	75.12	109.03
NaCl: 0.10148 normal at 4°. — Cell I. (May 8, 1902.)				280.7	0.07649	15.905	678.9
25.91	0.10114	75.35	108.75	218.8	0.08563	16.418	588.2
217.9	0.08556	16.524	584.9	139.2	0.09415	21.810	403.1
139.9	0.09395	21.787	404.4	25.91	0.10118	75.12	109.03
NaCl: 0.09990 normal at 4°. — Cell I. (June 18, 1902.)				NaCl: 0.09990 normal at 4°. — Cell II. (Jan. 15, 1903.)			
25.91	0.09957	76.44	108.88	25.94	0.09058	91.90	108.71
140.3	0.09248	22.018	406.5	305.7	0.07030	20.347	691.7
NaCl: 0.09990 normal at 4°. — Cell I. (June 19, 1902.)				25.94	0.09958	91.72	108.93
25.91	0.09957	76.28	109.10	(Jan. 17, 1903.)			
140.4	0.09248	21.926	408.2	25.94	0.09958	91.72	108.93
281.8	0.07500	16.226	678.0	(Jan. 17, 1903.)			
218.6	0.08428	16.701	587.4	305.2	0.07051	20.296	602.3
141.3	0.09241	21.965	407.8	25.94	0.09958	91.72	108.93
25.91	0.09957	76.23	109.19				
NaCl: 0.09990 normal at 4°. — Cell I. (May 15, 1902.)				NaCl: 0.09990 normal at 4°. — Cell I. (May 20, 1902.)			
25.92	0.009967	687.62	120.92	25.91	0.009967	687.90	120.85
138.9	0.009274	194.35	459.2	139.4	0.009267	193.20	462.3
218.9	0.008438	141.54	692.8	218.4	0.008440	141.70	691.4
(May 16, 1902.)				283.6	0.007441	131.62	843.3
25.91	0.009967	688.10	120.83	218.4	0.008440	141.86	691.4
139.1	0.009271	194.09	460.0	140.0	0.009261	193.59	461.7
218.4	0.008440	141.30	693.4	25.91	0.009967	688.28	120.80
(Feb. 21, 1903.)				NaCl: 0.009977 normal at 4°. — Cell II. (Feb. 20, 1903.)			
306.4	0.006950	156.50	901.7	306.7	0.006944	156.37	903.3
				26.00	0.009945	803.6	123.24

TABLE VI. — *Continued.*

NaCl: 0.0019980 normal at 4°. — Cell I. (May 10, 1902.)				NaCl: 0.0019978 normal at 4°. — Cell I. (May 9, 1902.)			
Tempera- ture.	Equivalents per Liter.	Resist- ance.	Equiv. Con- ductivity.	Tempera- ture.	Equivalents per Liter.	Resist- ance.	Equiv. Con- ductivity.
25.91	0.0019914	3322.2	124.91	25.91	0.0019913	3326.4	124.76
140.0	0.0018500	923.8	482.7	281.4	0.0014942	608.27	904.8
218.3	0.0016862	669.30	729.8	25.91	0.0019913	3314.3	125.05
281.5	0.0014945	608.90	903.6	138.0	0.0018518	927.3	497.9
218.3	0.0016862	669.04	730.1	217.7	0.0016851	669.60	729.8
140.2	0.0018501	921.0	483.8	25.91	0.0019913	3313.0	125.09
25.91	0.0019914	3310.8	125.18	NaCl: 0.0019954 normal at 4°. — Cell II. (March 8, 1902.)			
NaCl: 0.0020183 normal at 4°. — Cell I. (May 8, 1902.)				26.00	0.0019890	3926.0	125.65
25.91	0.0020116	3293.0	124.76	307.2	0.0013861	720.5	977.1
281.4	0.0015094	604.05	901.9	26.00	0.0019890	3909.4	125.87
25.91	0.0020116	3277.5	125.18	NaCl: 0.00049950 normal at 4°. — Cell I. (June 23, 1902.)			
NaCl: 0.00049950 normal at 4°. — Cell I. (June 23, 1902.)				25.91	0.0004979	12932.	127.31
25.91	0.0004979	12945.	127.18	141.3	0.0004621	3553.8	498.3
140.7	0.0004624	3563.7	496.6	219.3	0.0004213	2573.3	752.5
219.0	0.0004212	2565.3	755.0	281.6	0.0003733	2333.5	985.5
281.6	0.0003732	2333.4	935.0	219.5	0.0004213	2566.0	754.0
219.2	0.0004210	2570.6	753.3	142.3	0.0004616	3498.7	505.6
142.0	0.0004617	3357.8	499.3	25.91	0.0004979	12614.	129.84
25.91	0.0004979	12835.	127.67	NaCl: 0.00049820 normal at 4°. — Cell II. (March 18, 1902.)			
(June 26, 1902.)				26.00	0.00049874	15305.	127.05
25.91	0.0004979	12921.	127.42	306.8	0.00034719	2732.1	1013.9
281.3	0.0003736	2332.2	934.8	26.00	0.00049874	15163.	127.02
219.6	0.0004208	2564.9	755.4	KCl: 0.10014 normal at 4°. — Cell I. (Aug. 28, 1902.)			
139.3	0.0004630	3586.2	491.3	25.91	0.09972	63.30	131.29
25.91	0.0004979	12782.	128.15	141.7	0.09252	19.724	453.5
KCl: 0.10014 normal at 4°. — Cell I. (Aug. 28, 1902.)				(Sept. 27, 1902.)			
25.91	0.09972	63.17	131.56	25.91	0.09972	63.04	131.83
141.3	0.09256	19.780	452.5	281.2	0.07443	15.160	731.9
221.2	0.08404	15.380	640.6	KCl: 0.09992 normal at 4°. — Cell IIa. (Jan. 30, 1903.)			
282.4	0.07422	15.223	730.9	304.9	0.07046	19.094	729.1
221.2	0.08404	15.341	641.4	KCl: 0.09992 normal at 4°. — Cell II. (Feb. 13, 1903.)			
141.3	0.09256	19.701	453.9	25.94	0.09960	75.30	131.34
KCl: 0.10014 normal at 4°. — Cell I. (Sept. 2, 1902.)				(Feb. 16, 1903.)			
25.91	0.09982	63.30	131.15	305.3	0.07036	19.043	732.9
141.3	0.09254	19.783	452.1	KCl: 0.09992 normal at 4°. — Cell II. (Feb. 17, 1903.)			
218.2	0.08445	15.406	635.5	25.96	0.009972	681.8	144.87
141.9	0.09248	19.735	453.5	(March 28, 1903.)			
KCl: 0.09992 normal at 4°. — Cell II. (Feb. 10, 1903.)				26.00	0.009972	685.1	144.18
306.3	0.07015	19.068	733.4	KCl: 0.01004 normal at 4°. — Cell II. (Feb. 19, 1903.)			
25.94	0.09960	75.30	131.34	26.00	0.009972	685.1	144.18
KCl: 0.01004 normal at 4°. — Cell II. (Feb. 17, 1903.)				(Feb. 19, 1903.)			
304.7	0.007006	148.58	942.3	25.96	0.009972	681.8	144.87
(Feb. 18, 1903.)				(March 28, 1903.)			
306.0	0.006977	148.94	943.9	26.00	0.009972	685.1	144.18
25.96	0.009972	675.0	146.31				

TABLE VI.—*Continued.*

KCl: 0.0020007 normal at 4°.—Cell I. (Aug. 20, 1902.)				KCl: 0.0020007 normal at 4°.—Cell I. Aug. 25, 1902.			
Tempera- ture.	Equivalents per Liter.	Resist- ance.	Equiv. Con- ductivity.	Tempera- ture.	Equivalents per Liter.	Resist- ance.	Equiv. Con- ductivity.
25.91	0.0019943	2790.4	148.56	25.91	0.0019943	2785.6	148.82
140.3	0.0018527	828.0	537.9	140.1	0.0018530	824.8	539.9
218.4	0.0016885	618.9	788.3	219.0	0.0016869	616.1	792.6
282.0	0.0014942	574.0	959.1	281.5	0.0014963	573.6	958.4
218.5	0.0016885	619.3	787.7	219.3	0.0016861	617.2	791.5
140.4	0.0018527	824.7	539.9	140.5	0.0018522	820.8	542.6
25.91	0.0019943	2778.5	149.04	25.91	0.0019943	2726.8	151.87
KCl: 0.0019974 normal at 4°.—Cell II. (March 2, 1903.)				KCl: 0.00049990 normal at 4°.—Cell II. (March 20, 1903.)			
26.00	0.0019910	3308.6	149.02	26.00	0.00049830	12981.	150.32
306.6	0.0013900	685.8	1023.7	306.1	0.00034844	2611.3	1058.0
26.00	0.0019910	3298.0	149.18	26.00	0.00049830	12763.	151.70

second and third. All of the conductivity values are expressed in reciprocal ohms.

The agreement of the conductivity determinations made at different times, and often with different solutions, will be seen from this table. A comparison of the initial and final values in the separate experiments shows also the degree of contamination during the heating.

Table VIII contains a summary of the results given in Table VII. In deriving the means from the latter table, both the "initial" and "final" values have been included for the 0.1 and 0.01 normal solutions; but for the diluter solutions only the "initial" values have been considered; for, owing to contamination, the others are not equally reliable. The 18° values are those of Kohlrausch and Maltby.\* The values given in parentheses for zero concentration were obtained by extrapolation as described in Section XIII.

In order to compare the conductivity values at different temperatures, it is desirable to correct those directly measured for the change in concentration produced by the expansion when a given solution is heated. The values in Table VIII, which, owing to this expansion, refer at different temperatures to somewhat different concentrations, as is there indicated, have been reduced to the nearest round concentrations by a graphic interpolation with the help of the linear function  $\Lambda = \Lambda_0 - KCt$  (see Section XIII). The so-reduced values are presented in Table IX.

\* Wissenschaft. Abhandl. phys.-techn. Reichsanstalt, 3, 210 (1900).

TABLE VII.  
SUMMARY OF THE EQUIVALENT CONDUCTIVITY VALUES.

Date.	NaCl: 0.1 normal at 4°.							
	26° Init.	26° Fin.	140° Init.	140° Fin.	218° Init.	218° Fin.	281°.	306°.
Apr. 29, 1902	108.77	108.82	...	403.0	...	585.6	674.8	...
" 30, 1902	108.83	...	405.2	...	585.6	...	...	...
May 1, 1902	109.26	109.26	...	405.1	...	586.6	679.2	...
" 3, 1902	108.98	...	...	404.6	585.1	...	...	...
June 18, 1902	109.11	...	405.8	...	...	586.2	677.2	...
" 19, 1902	109.33	109.42	407.2	404.5	...	...	...	691.7
Jan. 15, 1903	108.87	109.09	...	...	...	...	...	692.3
" 17, 1903	109.09	...	...	...	...	...	...	...
" 17, 1903	...	109.09	...	...	...	...	...	...
NaCl: 0.01 normal at 4°.								
May 15, 1903	121.16	...	462.5	...	690.0	...	...	...
" 16, 1902	121.10	...	462.7	...	692.4	...	...	...
" 20, 1902	121.12	121.07	464.1	461.7	600.4	690.4	837.3	...
Feb. 20, 1903	...	...	...	...	...	...	...	901.6
" 21, 1903	...	...	...	...	...	...	...	900.7
NaCl: 0.002 normal at 4°.								
May 10, 1902	125.20	125.47	482.7	483.2	728.9	729.2	902.3	...
" 8, 1902	125.05	125.47	...	...	...	...	900.9	...
" 9, 1902	125.05	125.38	...	483.4	...	730.7	903.8	...
Mar. 3, 1903	125.65	125.87	...	...	...	...	...	974.0
NaCl: 0.0005 normal at 4°.								
June 23, 1902	127.48	127.97	494.3	492.7	751.7	749.3	933.7	...
" 25, 1902	127.61	130.14	494.0	498.0	748.2	749.0	933.7	...
" 26, 1902	127.72	128.45	...	493.6	...	750.1	933.9	...
Mar. 18, 1903	127.05	127.02	...	...	...	...	...	1011.5
KCl: 0.1 normal at 4°.								
Aug. 28, 1902	131.81	...	449.1	450.5	634.0	634.8	730.9	...
" 29, 1902	131.54	...	449.1	...	...	...	...	...
Sept. 2, 1902	131.40	...	448.2	448.6	635.1	...	731.9	...
" 27, 1902	132.08	...	...	...	...	...	...	...
Jan. 30, 1903	...	...	...	...	...	...	...	727.9
Feb. 10, 1903	131.51	...	...	...	...	...	...	733.7
" 13, 1903	131.51	...	...	...	...	...	...	...
" 16, 1903	...	...	...	...	...	...	...	732.1
KCl: 0.01 normal at 4°.								
Feb. 17, 1903	...	...	...	...	...	...	...	942.3
" 18, 1903	...	146.42	...	...	...	...	...	943.0
" 19, 1903	144.87	...	...	...	...	...	...	...
Mar. 28, 1903	144.18	...	...	...	...	...	...	...
KCl: 0.002 normal at 4°.								
Aug. 20, 1902	148.87	149.35	536.9	538.6	787.1	786.2	956.6	...
" 25, 1902	149.13	152.18	539.6	540.9	789.6	787.6	957.2	...
Mar. 2, 1903	149.02	149.18	...	...	...	...	...	1022.3
KCl: 0.0005 normal at 4°.								
Mar. 20, 1902	150.32	151.70	...	...	...	...	...	1057.7

TABLE VIII.

## FINAL VALUES FOR THE EQUIVALENT CONDUCTIVITY OF SODIUM AND POTASSIUM CHLORIDES.

Temperature.	NaCl		KCl	
	Equivalents per Liter.	Equivalent Conductivity.	Equivalents per Liter.	Equivalent Conductivity.
18°	0	(110.3)	0	(131.4)
	0.0005	107.18	0.0005	128.11
	0.002	105.55	0.002	126.31
	0.01	101.95	0.01	122.43
	0.1	92.02	0.1	112.08
140°	0	(512.)	0	(572.)
	0.000463	494.1	.....	....
	0.00185	482.7	0.00185	538.2
	0.00926	463.1	.....	....
	0.0952	405.2	0.098	449.1
218°	0	(782.)	0	(845.)
	0.000421	749.9	.....	....
	0.00169	728.9	0.00169	788.3
	0.00844	690.9	.....	....
	0.0868	585.8	0.0845	634.6
281°	0	(984.)	0	(1041.)
	0.000374	933.8	.....	....
	0.00149	902.3	0.00150	956.9
	0.00749	837.3	.....	....
	0.0774	677.1	0.0745	731.4
306°	0	(1078.)	0	(1125.)
	0.000348	1011.5	0.000349	1057.7
	0.00139	974.0	0.00139	1022.3
	0.00696	901.1	0.00699	943.1
	0.0705	692.0	0.0705	731.2

TABLE IX.

THE EQUIVALENT CONDUCTIVITY AT ROUND CONCENTRATIONS.

Substance.	Equivalents per Liter.	18°.	140°.	218°.	231°.	306°.
NaCl	0	(110.3)	512	782	984	1078
"	0.0005	107.18	493	747	926	1004
"	0.002	105.55	482	726	893	960
"	0.01	101.95	461	686	830	878
"	0.1	92.02	403	577	656	643
KCl	0	(131.4)	572	845	1041	1125
"	0.0005	128.11	...	...	...	1051
"	0.002	126.31	538	786	950	1007
"	0.01	122.43	...	...	...	922
"	0.1	112.03	447	620	699	686

## XIII. THE CHANGE OF CONDUCTIVITY WITH THE CONCENTRATION.

It is a well-known fact that the Mass-Action Law does not express even approximately the change with the concentration of the dissociation of salts and strong acids and bases, when this, in accordance with the Ionic Theory, is calculated from the conductivity ratio  $\Lambda/\Lambda_0$ . This has led to the proposal of numerous other functions,\* some of them derived inductively and others through hypothetical considerations, which have for their purpose an accurate representation of the experimental conductivity values and the dissociation values deduced therefrom. The extended discussion of the matter has not yet led to any conclusion as far as the theoretical explanation of the phenomenon is concerned. There have, however, been discovered some simple empirical formulas which at ordinary temperatures express the observed results satisfactorily.

Those which contain only a single arbitrary constant have the following form when expressed in terms of the equivalent conductivity ( $\Lambda$ ) at

\* Compare Kohlrausch, Wied. Ann., **26**, 200 (1885); **50**, 394 (1893); MacGregory, ibid., **51**, 183 (1894); Barmwater, Ztschr. phys. Chem., **28**, 134, 428 (1890); Sabat, ibid., **41**, 224 (1902); Muller, Compt. rend., **128**, 505 (1899); Kohlrausch, Sitzungsber. preus. Akad., **44**, 1002 (1900); Rudolph, Ztschr. phys. Chem., **17**, 385 (1895) van't Hoff, ibid., **18**, 300 (1895); Kohlrausch, ibid., **18**, 602 (1895); Storch, ibid., **19**, 13 (1896); Bancroft, ibid., **31**, 188 (1899); Jahn, ibid., **37**, 499 (1901); **41**, 265, 288 (1902); Nernst, ibid., **38**, 493 (1901).

any concentration  $C$  and the limiting conductivity  $\Lambda_0$  at zero concentration :

$$\frac{\Lambda_0 - \Lambda}{C^{\frac{1}{2}}} = K \text{ (Kohlrausch),}$$

$$\frac{\Lambda_0 - \Lambda}{\Lambda^{\frac{1}{2}} C^{\frac{1}{2}}} = K \text{ (Barmwater),}$$

$$\frac{\Lambda_0 - \Lambda}{\Lambda^{\frac{3}{2}} C^{\frac{1}{2}}} = K \text{ (van't Hoff),}$$

$$\frac{\Lambda_0 - \Lambda}{\Lambda^2 C^{\frac{1}{2}}} = K \text{ (Rudolphi).}$$

It seemed therefore to be of especial interest to test the applicability of these formulas at the widely different temperatures employed in our experiments. In making such a test, it must be borne in mind that the results will be in a high degree dependent on the values of  $\Lambda_0$  employed, since in dilute solutions  $\Lambda_0 - \Lambda$  is a relatively small quantity; yet in several instances authors have not given sufficient consideration to this matter. The most satisfactory method of procedure seems to us to be the elimination of the  $\Lambda_0$  value, which cannot be determined with sufficient accuracy by extrapolation, by writing the functions in the following form :

$$\Lambda = \Lambda_0 - K C^{\frac{1}{2}} \text{ (Kohlrausch),}$$

$$\Lambda = \Lambda_0 - K \Lambda^{\frac{1}{2}} C^{\frac{1}{2}} \text{ (Barmwater),}$$

$$\Lambda = \Lambda_0 - K \Lambda^{\frac{3}{2}} C^{\frac{1}{2}} \text{ (van't Hoff),}$$

$$\Lambda = \Lambda_0 - K \Lambda^2 C^{\frac{1}{2}} \text{ (Ostwald),}$$

and then plotting the values of  $\Lambda$  along one co-ordinate axis and those of the  $C-\Lambda$  function constituting the last term (that is,  $C^{\frac{1}{2}}$ ,  $\Lambda^{\frac{1}{2}} C^{\frac{1}{2}}$ , etc.) along the other axis, as is illustrated by Figure 9. If the function in question holds, the points will of course lie upon a straight line; and by comparing, in the case of the different functions, the deviations of the separate points from the best representative straight line that can be drawn, a measure of the degree of applicability of each function is obtained. All our complete series of measurements and those of Kohlrausch and Maltby on the same salts at 18° have been studied in this way, a plot on a very large scale being employed. The straight lines were drawn in every case so as to make the percentage deviations of the two conductivity values for the two more concentrated solutions and

TABLE X.—DEVIATION OF THE OBSERVED CONDUCTIVITY VALUES FROM THOSE CALCULATED BY VARIOUS EMPIRICAL FORMULAS.

Salt and Temperature.	Milli-Equivalents per Liter.	Equivalent Conductivity.	Percentage Deviation of Observed from Calculated Conductivity Values.			
			$C^{\frac{1}{2}}$ .	$\Delta^{\frac{1}{2}} C^{\frac{1}{2}}$ .	$\Delta^{\frac{3}{2}} C^{\frac{1}{2}}$ .	$\Delta^2 C^{\frac{1}{2}}$ .
NaCl 18°	0.5	107.18	-0.16	-0.17	+0.08	+0.04
	2.0	105.55	+0.08	+0.11	-0.06	-0.06
	10.0	101.95	+0.09	+0.15	-0.17	-0.24
	100.0	92.02	-0.16	-0.24	+0.11	+0.18
	Mean . . .	0.12	0.17	0.09	0.18	
NaCl 140°	0.463	496.3	+0.24	+0.12	+0.28	+0.41
	1.85	488.5	-0.25	-0.21	-0.62	-0.42
	9.26	464.8	+0.02	+0.19	-0.44	-0.05
	95.2	407.3	-0.02	-0.15	+0.37	+0.05
	Mean . . .	0.13	0.17	0.43	0.23	
NaCl 218°	0.421	753.8	+0.05	-0.07	+0.28	+0.16
	1.69	732.4	-0.04	+0.11	-0.20	-0.08
	8.44	693.5	-0.18	+0.04	-0.34	+0.08
	86.8	588.3	+0.18	-0.03	+0.52	-0.03
	Mean . . .	0.11	0.06	0.34	0.09	
NaCl 281°	0.374	937.6	+0.01	-0.18	+0.11	-0.18
	1.49	906.2	-0.02	+0.17	-0.05	+0.11
	7.49	840.9	-0.60	-0.15	-1.43	+0.28
	77.4	680.1	+0.50	+0.14	+0.48	-0.46
	Mean . . .	0.28	0.16	0.27	0.26	
NaCl 306°	0.348	1013.	-0.05	-0.17	-0.14	-0.02
	1.39	975.2	+0.05	+0.14	+0.11	+0.02
	6.96	902.2	+0.84	+1.20	+1.50	+3.54
	70.5	686.0	-0.45	-1.31	-1.68	-2.84
	Mean . . .	0.22	0.71	0.76	1.61	
KCl 18°	0.5	128.11	-0.08	-0.10	+0.12	+0.07
	2.0	126.31	+0.04	+0.09	-0.11	-0.05
	10.0	122.43	-0.08	+0.05	-0.40	-0.70
	100.0	112.03	+0.06	-0.02	+0.58	+0.90
	Mean . . .	0.06	0.07	0.30	0.43	
KCl 306°	0.349	1050.	-0.21	-0.45	-0.22	-0.60
	1.39	1024.	+0.18	+0.41	+0.29	+0.49
	6.99	945.8	+0.05	+0.80	+0.90	+2.01
	70.5	732.1	-0.05	-0.67	-0.95	-2.44
	Mean . . .	0.12	0.58	0.59	1.38	

also of those for the two more dilute solutions opposite and nearly equal. The results are presented in detail and in summarized form in Tables X and XI. The concentration is expressed in milliequivalents per liter. The numbers in the last four columns show the percentage difference between the observed conductivity and that required by the assumed linear function, the nature of whose argument ( $C^{\frac{1}{2}}$ ,  $C^{\frac{1}{2}}\Delta t$ , etc.) is shown by the headings.

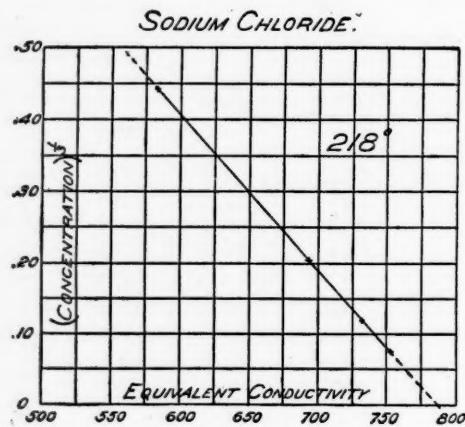


FIGURE 9.

TABLE XI.  
SUMMARY OF THE MEAN DEVIATIONS.

Salt.	Temp.	$C^{\frac{1}{2}}$	$\Delta \frac{1}{2} C^{\frac{1}{2}}$	$\Delta \frac{3}{2} C^{\frac{1}{2}}$	$\Delta^2 C^{\frac{1}{2}}$
NaCl	18°	0.12	0.17	0.09	0.13
"	140°	0.13	0.17	0.43	0.23
"	218°	0.11	0.06	0.34	0.09
"	281°	0.28	0.16	0.27	0.26
"	306°	0.22	0.71	0.76	1.61
KCl	18°	0.06	0.07	0.30	0.43
"	306°	0.12	0.58	0.59	1.38
Mean . . .		0.15	0.27	0.40	0.59

An examination of Table XI leads to the following conclusions: All four formulas express fairly well the results with sodium chloride at 18°; but the formulas of van't Hoff and of Rudolphi do not apply well

to those with potassium chloride at  $18^{\circ}$ . The Kohlrausch formula expresses the results for both salts at all temperatures without great error,\* and the same is true of the Barmwater formula, except at the highest temperature, where the deviations with both salts are large. The van't Hoff and Rudolphi formulas do not accord at all with the observed values at  $306^{\circ}$ , the deviations in the case of the latter formula being especially large, while at the lower temperatures of 140, 218, and  $281^{\circ}$  the van't Hoff formula is far less satisfactory than those of Kohlrausch and Barmwater. On the whole, therefore, the simple Kohlrausch formula furnishes the best representation of the results, and the Barmwater the next best,—facts which are directly indicated by the final means at the foot of the last table. Whether within the range of concentration in question (0.0005—0.1 normal) the deviations corresponding to the former are really less than the experimental errors cannot be decided with certainty: the greatest deviation (see Table X) from the very accurate values of Kohlrausch and Maltby at  $18^{\circ}$  is 0.13 per cent † in the case of sodium chloride, and 0.06 per cent in that of potassium chloride; the greatest deviations at the highest temperatures are 0.55 per cent at  $281^{\circ}$  and 0.40 per cent at  $306^{\circ}$  in the case of sodium chloride, and only 0.20 per cent at  $306^{\circ}$  in that of potassium chloride. It seems improbable that the experimental errors are as large as these deviations in the case of the sodium chloride; but it is perhaps not impossible.

It may be of interest to state also the percentage deviations of our straight line corresponding to the Kohlrausch function from the points representing the conductivities of sodium and potassium chloride at  $18^{\circ}$  in the still more dilute solutions investigated by Kohlrausch and Maltby. These deviations are —0.53 and —0.42 per cent, respectively, in case of the 0.0001 normal solutions, and —0.36 and —0.25 per cent, respectively, in that of the 0.0002 normal solutions. It is to be noted with reference to the significance of this disagreement, that the conductivity of the water used for the 0.0001 normal solutions formed from 7 to 10 per cent of that of the salt, and that the results were corrected for it under the assumption that it was uninfluenced by the addition of the salt. Kohlrausch and Maltby, however, consider it almost impossible that from this source an error of the magnitude of these deviations can arise.

\* Compare also Fig. 9, which is an accurate plot of the values for sodium chloride at  $218^{\circ}$ .

† Assuming the first two as well as the last two deviations to have been completely equalized, which could have been done by slightly displacing the representative straight line.

The at least approximate validity of the simple Kohlrausch equation under such widely different conditions, is a fact that must receive attention in any theoretical explanation of the phenomenon. The fact seems somewhat remarkable when it is considered how great the change is in the state of the solvent, which has been raised from near its melting point to not very far below its critical point, and when it is considered that the dissociation has decreased in the 0.1 normal solutions from about 84 per cent at 18° to 60 per cent at 306° (see Section XV). The equation cannot, however, retain its validity as the dissociation tendency approaches zero; for then with increasing concentration the calculated values of  $\Lambda$  would soon become negative: it must, if it is to apply generally, be modified by multiplying the cube-root of the concentration by some function of  $\Lambda$  which does not vary much as long as  $\Lambda/\Lambda_0$  is large, in a manner similar to that which has been proposed by Barmwater.

The fact that the van't Hoff equation does not express satisfactorily the results with many salts even at 18° (see KCl in Table X) has led to the suggestion by Storch and Bancroft that a general expression of the form  $\Lambda_0 - \Lambda = KA^nC^{n-1}$  be employed, the exponent  $n$  being different with each salt. Our results show that in order to attain agreement it would be necessary to vary the value of  $n$  also with the temperature. Thus it was found that by putting  $n = 1.6$ , the results with sodium chloride at 306° are expressed with a mean deviation of only 0.15 per cent, but the use of this same exponent with the results at 18° gives rise to a mean deviation of 0.69 per cent, while as shown in the above tables, the van't Hoff function, with  $n = 1.5$ , applies well at 18°, but fails at 306°. The fact that even at the highest temperature the exponent required has risen only to 1.6 shows that the results do not correspond much more closely with the Mass-Action Law, which requires the exponent 2, than they do at the ordinary temperature.

In view of the foregoing considerations there is at present no more reliable means of deriving the conductivity  $\Lambda_0$  for zero concentration from our results at the higher temperatures than by the application of the Kohlrausch equation. We have therefore determined from our plots the intercept of the straight line representing this equation with the axis along which the conductivity values are laid off; and it is these values of  $\Lambda_0$  which are recorded within parentheses in Table VIII. For the sake of uniformity, the  $\Lambda_0$  values at 18° were derived in the same way from the data of Kohlrausch and Maltby; they are about 1.2 per cent larger than those deduced by these investigators.

## XIV. CHANGE OF THE CONDUCTIVITY WITH THE TEMPERATURE.

In order to show more clearly the effect of temperature on the conductivity, the values of Table IX are represented graphically in Figures 10 and 11. (The dotted curve for the 0.5 normal sodium chloride solution is based on values extrapolated from 0.1 normal by means of the Kohlrausch linear equation, and it has been drawn only to indicate roughly the general character of the curve at a higher concentration.)

A consideration of these plots and of the data themselves leads to the somewhat striking conclusion that throughout this wide range of temperature of nearly  $300^{\circ}$ , the conductivity extrapolated for zero concentra-

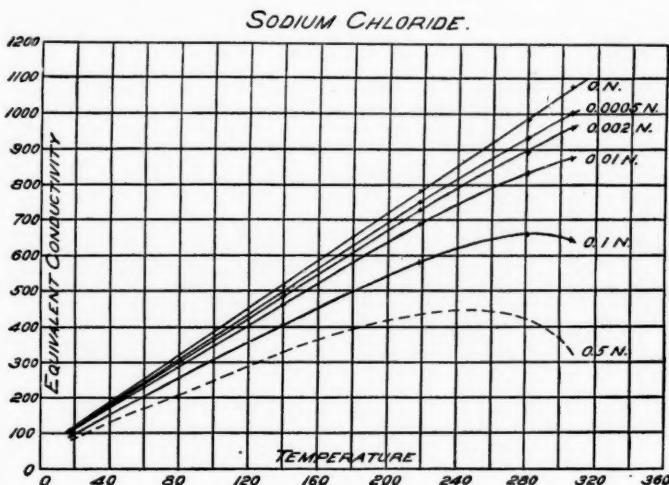


FIGURE 10.

tion, and therefore the migration velocity of the ions, increases in the case of sodium chloride at a rate closely proportional to the increase of temperature. In the case of potassium chloride this principle expresses the results without considerable error up to  $218^{\circ}$ , but at the higher temperatures the conductivity increases somewhat more slowly than it requires.

To show the extent of the deviations, the conductivity has been expressed by a linear equation of the form:  $(\Lambda_0)_t = (\Lambda_0)_{18} + a(t - 18)$ . The value (3.34) adopted for  $a$  in the case of the sodium chloride was

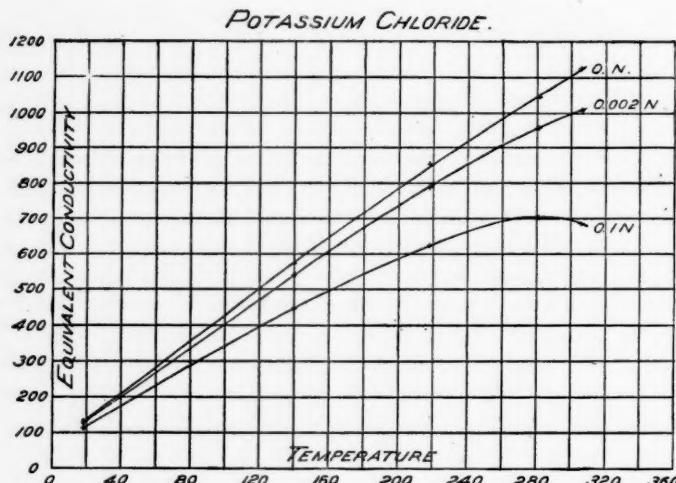


FIGURE 11.

the mean of that derived by using the values of  $\Lambda_0$  at 18 and 281° and at 18 and 306°. The value of 3.57 in the case of potassium chloride was calculated from the values of  $\Lambda_0$  at 18° and 218°. The values of  $\Lambda_0$  calculated from these equations are given in the following table beside those previously found.

TABLE XII.

THE  $\Lambda_0$  VALUES AS A LINEAR TEMPERATURE FUNCTION.

Temper- ature.	Sodium Chloride.			Potassium Chloride.		
	Found.	Calculated.	Per cent. Diff.	Found.	Calculated.	Per cent. Diff.
18°	110	...	...	131	...	...
140°	512	517	-1.0	572	566	+0.7
218°	782	778	+0.5	845	845	...
281°	984	988	-0.4	1041	1070	-2.7
306°	1078	1072	+0.6	1125	1159	-2.9

It will be seen that the differences in the case of sodium chloride are in opposite directions at 140 and 218°; they are therefore doubtless in large part, if not entirely, due to experimental errors; and therefore, within the limits of these, the conductivity at infinite dilution is a linear function of the temperature in the case of this salt.\* With potassium chloride the deviation at 140°, though probably real, since it falls upon the smooth curve drawn through all the values, amounts to only 0.7 per cent. At the higher temperatures the deviations are seen to be much larger, though still of secondary magnitude. This approximate proportionality between the increase of migration velocity and that of the temperature has, up to 100°, already been observed by Schaller.†

The values of the percentage temperature-coefficients referred to the value at 18°  $\left( \frac{100 \Delta \Lambda_0}{(\Lambda_0)_{18} \Delta t} \right)$  are 2.74 for potassium chloride (between 18 and 218°) and 3.05 for sodium chloride. These are much higher than those observed on dilute solutions (0.01—0.001 normal), by Kohlrausch between 18 and 26° (2.21 and 2.38), by Dégusne between 18 and 34° (2.28 and 2.40), by Arrhenius between 18 and 52° (2.33 and 2.53), and by Krannhals between 18 and 99.4° (2.40 and 2.62)‡. This is due in part to the facts that the values of some of these investigators were not corrected for the expansion of the solutions upon heating and that they refer to solutions not infinitely dilute; § but it also undoubtedly arises in part from the fact that the temperature function is not perfectly linear until temperatures considerably above 18° are reached.

The ratio of the limiting conductivity of potassium chloride to that of sodium chloride is 1.19 at 18°, 1.13 at 140°, 1.08 at 218°, 1.06 at 281°, and 1.04 at 306°. The migration-velocities of the potassium and sodium ions are therefore slowly approaching equality.

The conductivity curves (see Figs. 10 and 11) at the higher concentrations recede more and more from that for zero concentration as the temperature rises, owing to a decreasing dissociation tendency (see

\* This is also clearly shown by the values of  $a$  calculated for the four successive temperature-intervals 18—140, 140—218, 218—281, and 281—306°; these are 3.30, 3.47, 3.21, and 3.75 (this last value being much in error because the interval is small).

† Ztschr. phys. Chem., **25**, 512, 523 (1898).

‡ These data are taken from Kohlrausch and Holborn's Leitvermögen der Elektrolyte, 197-199.

§ Thus, the temperature-coefficient between 18° and 140° of our 0.01 normal NaCl solutions is 2.90, while that at infinite dilution is 3.05.

Section XV). This even gives rise to a maximum value in the case of the 0.1 normal solution of both salts at a temperature of about 280°. With more concentrated solutions this effect would undoubtedly be much more pronounced, as is indicated by the dotted curve in Fig. 10.

#### XV. CHANGE OF THE DISSOCIATION WITH THE CONCENTRATION AND TEMPERATURE.

It has already been shown in Section XIII that the conductivity  $\Lambda$  changes with the concentration  $C$  at all temperatures closely in accordance with the equation  $\Lambda_0 - \Lambda = K C^{\frac{1}{3}}$ . Expressed in terms of the dissociation,  $x = \frac{\Lambda}{\Lambda_0}$ , this becomes  $\frac{1-x}{C^{\frac{1}{3}}} = K$ ; that is, the fraction of the salt undissociated is directly proportional to the cube-root of the concentration, or the concentration of the undissociated molecules,  $(1-x)C$ , is directly proportional to the  $\frac{1}{3}$  power of the total concentration.

The change of the degree of dissociation with the temperature is shown for both salts in Table XIII, and for sodium chloride in Fig. 12.

TABLE XIII.  
DISSOCIATION.

Substance.	Equivalents per Liter.	18°	140°	218°	281°	306°
NaCl	0	100.0	100.0	100.0	100.0	100.0
"	0.0005	97.3	96.6	95.8	94.3	93.2
"	0.002	95.7	94.5	93.0	91.0	89.1
"	0.01	92.5	90.3	87.9	84.5	81.4
"	0.1	83.4	79.0	74.0	66.8	59.8
KCl	0	100.0	100.0	100.0	100.0	100.0
"	0.0005	97.5	...	...	...	93.4
"	0.002	96.1	94.1	92.7	91.3	89.5
"	0.01	93.2	...	...	...	82.0
"	0.1	85.2	78.3	73.3	67.2	61.0

It will be seen that, especially in the 0.1 normal solution, the dissociation has decreased very greatly at the higher temperatures, namely, from 83–85 per cent at 18° to 60–61 per cent at 306°; and that the decrease is becoming extremely rapid at those temperatures, the course of the curve indicating that the dissociation is very small in the neighborhood of the critical temperature (about 360°).

Table XIII also shows that the dissociation values for the two chlorides are nearly identical at all temperatures and concentrations, the extreme variation being about 2 per cent in the 0.1 normal solution. This gives support to the idea that the decrease of conductivity and of the calculated dissociation is due to a physical cause (probably in some way to the electrical charges on the ions) and not to specific chemical affinity. The theoretical discussion of the results is, however, best postponed until we have made more extended series of measurements.

### SODIUM CHLORIDE.

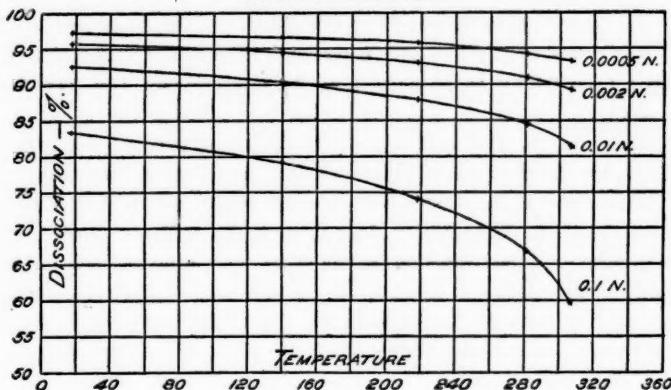


FIGURE 12.

The values of the constant  $K$  in the equation  $(1 - x) = KC^{\frac{1}{2}}$  are tabulated below, as these give a measure of the dissociation-tendency independent of the concentration. They were obtained from the plots described in Section XIII by taking the ratio  $\left( \frac{\Delta\Lambda}{\Delta C^{\frac{1}{2}}} \right)$  of the intercepts on the two axes, of the best representative straight line, and dividing this ratio by  $\Lambda_0$ .

TABLE XIV.  
VALUES OF THE DISSOCIATION CONSTANT  $(1 - x) / C^{\frac{1}{2}}$ .

Salt	18°	140°	218°	281°	306°
NaCl	0.366	0.448	0.573	0.745	0.877
KCl	0.321	0.468	0.577	0.713	0.853

## XVI. SUMMARY.

In this article has been described the construction of a platinum-lined bomb of 124 ccm. capacity with electrodes insulated by quartz-crystal cylinders, by means of which the conductivity and specific volume of aqueous salt solutions can be determined with an accuracy of 0.2 or 0.3 per cent, at least up to a temperature of 306°. The methods employed for overcoming the serious mechanical difficulties may be of assistance in other investigations requiring similar apparatus; for instance, in calorimetric bomb work.

Measurements of the conductivity and specific volume have been made upon solutions of sodium and potassium chlorides at concentrations varying from 0.0005 to 0.1 normal, at the temperatures 140, 218, 281, and 306°.

The results obtained with these salts show that even at the highest temperature the dissociation calculated from the conductivity ratio does not change with the concentration in much closer accord with the requirements of the Mass-Action Law than at the ordinary temperature. The various empirical functions which have been proposed for the expression of the change of conductivity with the concentration were tested as to their applicability to the results at these widely different temperatures by a graphical method by which the effect of the uncertainty in the conductivity values ( $\Lambda_0$ ) for zero concentration was eliminated. It was found that that given by Kohlrausch,  $\Lambda_0 - \Lambda = KC^{\frac{1}{2}}$ , was most satisfactory, the deviations being scarcely greater than the possible experimental error. Except at the highest temperature, the function of Barmwater,  $\Lambda_0 - \Lambda = K \Lambda^{\frac{1}{2}} C^{\frac{1}{2}}$ , also gave good results. To make applicable the general function  $\Lambda_0 - \Lambda = K \Lambda^n C^{n-1}$  (of which the van't Hoff function  $\Lambda_0 - \Lambda = K \Lambda^{\frac{1}{2}} C^{\frac{1}{2}}$  is a special case), it is necessary to vary the exponent  $n$  not only with the nature of the salt, but also with the temperature.

The conductivity values extrapolated for infinite dilution, and therefore the migration-velocities of the ions, were found to be an approximately linear function of the temperature, throughout the whole range of temperature in the case of sodium chloride, and up to 218° in the case of potassium chloride, the deviations being moreover not very large (3.5 per cent) even at the highest temperatures with the latter salt. The temperature-coefficients referred to the values at 18° are 3.05 per cent for sodium chloride between 18 and 306°, and 2.74 per cent for potassium chloride between 18 and 218°.

The ratio of the conductivities of potassium and sodium chlorides at infinite dilution decreases from 1.19 at  $18^{\circ}$  to 1.04 at  $306^{\circ}$ , showing that the migration velocities of the sodium and potassium ions are slowly approaching equality.

The degrees of dissociation of the two salts are nearly identical (extreme variation about 2 per cent) at all temperatures and concentrations. The dissociation in 0.1 normal solution has approximately the following values: 84 per cent at  $18^{\circ}$ , 79 per cent at  $140^{\circ}$ , 74 per cent at  $218^{\circ}$ , 67 per cent at  $281^{\circ}$ , and 60 per cent at  $306^{\circ}$ . It is decreasing with great rapidity at the higher temperatures. Its change with the concentration is at all temperatures accurately expressed by the equation  $(1 - x) / C^{\frac{1}{2}} = K$ .

The conductivity of the vapor over a 0.1 normal potassium chloride solution at  $306^{\circ}$  is too small to be observed with the present apparatus: its specific conductivity is certainly less than  $\frac{1}{200000}$  part of that of the liquid.

The specific volume of the 0.002 normal solutions, which can be regarded as identical with that of pure water, was found to be 1.186 at  $218^{\circ}$ , 1.336 at  $281^{\circ}$ , and 1.434 at  $306^{\circ}$ . The expansions of the two 0.1 normal solutions are substantially identical, but somewhat less than that of water, as is shown by the fact that the ratio of their specific volumes at  $306^{\circ}$  and  $4^{\circ}$  is 1.422, instead of 1.434.

This investigation is being continued with the co-operation of others. During the coming year other di-ionic salts and some tri-ionic salts will be investigated in the same manner. A separate research will deal with weak acids and their neutral salts with the aim of studying hydrolysis and the dissociation-constant of water. Another line of work to be carried out with the bomb will consist in the determination of the dielectric constant of water up to  $306^{\circ}$ . Then the attempt will be made to extend all these measurements to the critical temperature.

SEPTEMBER, 1903.